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METHODS FOR SIMULATING GAS PHASE SO_2 OXIDATION IN
ATMOSPHERIC MODELS

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16. ABSTRACT Two different approaches are presented for simulating gas phase sulfur dioxide oxidation in atmospheric models. The first approach was to develop an empirical relationship based on rate data collected at four coal-fired power plants during 11 separate studies. Cosine functions were used to simulate annual and diurnal variations in the oxidation rate constant. The time variant rate constant was superimposed on a constant rate coefficient of 0.002 h⁻¹ used for nonsunlight hours. The model predicts a maximum (solar noon) rate constant of 0.0285 h⁻¹ for mid-July. The second approach was to develop a kinetic model based on data obtained from smog chamber experiments using mixtures of sulfur dioxide propene, butane, nitrogen oxides, and water vapor. Sulfur dioxide oxidation in the gas phase was found to occur by two mechanisms. At low HC/NO_x values hydroxyl radical addition to sulfur dioxide predominates. At high HC/NO_x values, oxidation via reaction with products of the ozone-olefin reaction dominates. The chamber data suggest that the HO-SO₂ reaction leads mainly to the production of hydroperoxyl radical and sulfuric acid. A previously proposed mechanism for the reaction of sulfur dioxide with Criegee intermediates was found to provide an excellent fit to the data at the high HC/NO_x values.		
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ABSTRACT

Two very different schemes are presented for the simulation of gas phase SO_2 oxidation in atmospheric models.

Rate data collected at four coal-fired power plants during 11 separate studies were used to develop an empirical model. Simple cosine functions were used to simulate the annual and diurnal variation in the SO_2 oxidation rate constant. This time-variant rate constant was superimposed onto a constant rate coefficient ($k_0 = 0.002 \text{ h}^{-1}$) that was used for non-daylight hours. The equation, which resulted from fitting this function to the field measurements, reproduces the diurnal and seasonal trends and explains the bulk (56%) of the observed variability. The model predicts a maximum (solar noon) rate constant of 0.0285 h^{-1} for mid-July.

Data obtained from a series of smog chamber experiments using mixtures of SO_2 , propene, butane, NO_x and H_2O were used to develop a kinetic model. Sulfur dioxide oxidation in the gas phase was found to proceed by two predominant mechanisms. At low hydrocarbon/ NO_x ratios, the reaction is dominated by HO addition to SO_2 . At high hydrocarbon/ NO_x ratios, oxidation via reaction with products of the O_3 -olefin reaction dominates. The chamber data suggests that the $\text{HO} + \text{SO}_2$ reaction leads predominantly to the production of HO_2 radicals and H_2SO_4 . A previously proposed mechanism for reaction of SO_2 with Criegee intermediates was found to provide an excellent fit to the experimental data at high hydrocarbon/ NO_x ratios.

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INTRODUCTION

During the past decade, an enormous amount of effort has been directed toward the measurement of the rate and determination of the mechanism of sulfur dioxide (SO_2) oxidation in the atmosphere. This effort has been sustained by a concern for a wide variety of environmental impacts attributed to SO_2 and the sulfate (SO_4^{2-}) aerosols that result from the chemical transformation.

Although SO_2 oxidation is undoubtedly a composite of gas and liquid phase reactions, the bulk of the field and laboratory data available is applicable only to the gas phase. Studies of droplet oxidation have just begun and we have only a primitive understanding of the controlling processes in cloud systems. The chemical mechanism and mathematical models discussed herein deal exclusively with gas phase SO_2 oxidation.

Mathematical models that are used to simulate the conversion of SO_2 to SO_4^{2-} in the atmosphere fall into two broad classes:

1. Empirical Models - As the name suggests, these models are based on experimental data with some sort of statistical averaging to remove some of the variability inherent in field measurements of SO_2 oxidation rates. The rate is usually assumed to be first order in SO_2 .
2. Kinetic Models - In this approach, a chemical mechanism is developed to describe SO_2 oxidation in terms of elementary reactions. Laboratory-measured rate parameters for these reactions are used in mathematical expressions that describe the time dependence of the major species.

The approach that is chosen for a particular transport/transformation model depends, to a large extent, on the model's proposed applications. Empirical models, because of their parameterization, represent average conditions and thus should not be expected to exhibit significant skill in an event calculation. Their predictive ability will be acceptable only if the data base used to develop the model is representative of the conditions for which the predictions are to be made. To their advantage, however, empirical models require a minimum of input and computation; thus, a large number of cases can be easily simulated, once again enhancing the results for longer term averages.

Kinetic schemes borrow heavily on the smog/ozone models developed for urban areas. Free radical photochemistry is described by a mechanism comprised of a series of typically 50-150 elementary reactions. These models contain significantly more chemical "sense" and can be expected to respond to short-term variations in meteorology and radical precursor emissions. The price for this capability is considerable. Input requirements are staggering. Data are needed on solar spectrum and intensity, temperature, humidity, and ideally source terms on an hour-by-hour basis for the major precursors (NO_x , SO_2 , hydrocarbons)

as well as information on the hydrocarbon distribution. A set of simultaneous differential equations, one for each species, must be solved at each time step. This places an extreme computational burden on the model that may limit the number of simulations that can be executed for a particular assessment.

In the following report, various empirical and kinetic schemes that have been developed to describe SO_2 oxidation will be discussed. Alternative schemes will be described. These alternatives have been developed using recent field and laboratory data, much of which was not available to previous modelers. It is not intended that this report provide a comprehensive review and evaluation of empirical and kinetic chemical models; rather, it is our intention to provide new reliable schemes based on the best data bases available.

EMPIRICAL MODEL

The current proliferation of long-range transport models has led to a wide variety of schemes for the parameterization of the SO_2 oxidation rate constant. Techniques for trajectory models vary from the use of time invariant values for the rate constant (e.g., Fay and Rosenzweig, 1980) to values that are allowed to vary diurnally and seasonally (e.g., Shannon, 1981). These approximation procedures are based only loosely on field data and, in many cases, represent "best fits" to monitoring data using the model under development.

Wilson (1981) has reviewed the data collected in 12 power plants and smelter studies conducted between 1974 and 1979. His analysis of this diverse data base has demonstrated the importance of time of day as a factor affecting the observed rate constant. Of particular interest is the good correlation ($r = 0.64$) which was obtained between the percentage sulfur in the particulate form (SP/ST, %) and total solar radiation dose ($\text{KW} \cdot \text{h}/\text{m}^2$). A linear fit to the data (excluding the VISTTA data from the Navajo Power Plant) yield the following relationship:

$$\frac{\text{SP}}{\text{ST}} (\%) = 3.66 (\text{Average Solar Radiation, KW/m}^2)(\text{time, h}) - 0.84 \quad (\text{I})$$

The observed relationship offers the opportunity to apply data obtained under a wide range of meteorological and source conditions to a systematic estimation of the SO_2 conversion rate. However, the relationship is only useful if reliable solar intensity data are available or can be predicted for situations under study.

A more elaborate parameterization scheme has been proposed by Gillani et al. (1981) for dry conditions. This treatment must, in fact, be classified as semi-empirical since it combines a fit to field data with assumptions regarding the chemical processes. Based on the analysis of two sets of field measurements at the Labadie Power Plant taken on September 7, 1976, and August 7, 1976, the authors obtained the following relationship:

$$(k_t)_d = (0.03 \pm 0.01)(R \cdot H \cdot [O_3]_o) \quad (\text{II})$$

where

$(k_t)_d \equiv$ the dry atmosphere rate constant ($\% \text{ h}^{-1}$)

$R \equiv$ solar radiation in (KW m^{-2})

$H \equiv$ mixing height in (m)

$[O_3]_o \equiv$ background ozone concentration (ppm)

This procedure shows great promise and excellent agreement is obtained for these experiments in which the chemistry is known to be dominated by dry processes. The parameterization is based on a very limited data base, however, and requires more input parameters than other techniques.

Perhaps the most striking feature of field measurements of the SO_2 oxidation rate constant is the variability in the data. Measured rate constants range from 0.0 to $> 0.1 \text{ h}^{-1}$, sometimes at the same location and within a period of a few days. There are, however, several features of the data that provide reason for optimism. The most striking of these are the diurnal and seasonal trends.

DIURNAL VARIATIONS

The diurnal variation in the measured SO_2 rate constant was first reported by Husar et al. (1978). Additional studies of the diurnal variation have been reported by Forrest et al. (1981), Gillani et al. (1981), and Bailey et al. (1982). These data are presented in Figure 1.

In each case, the maximum rate constant ($0.02\text{--}0.08 \text{ h}^{-1}$) was observed for measurements made near solar noon. Nighttime rate constants are generally less than 0.005 h^{-1} with intermediate values during morning and afternoon hours. It is not possible to associate this diurnal trend with the change in a single meteorological variable. Several meteorological parameters (e.g., solar intensity, temperature, humidity, and atmospheric mixing rate) exhibit similar cycles. Convincing arguments can be made why each, or any combination of these variables, could produce the observed diurnal cycle in the SO_2 oxidation rate constant.

All of the above studies were performed during summer and early fall. There have been very few data reported that specifically address diurnal variations in SO_2 oxidation during the winter months. However, there is limited information available from a field study conducted by TVA in the winter of 1975-1976 (Meagher et al., 1978). The diurnal trend is much less pronounced in these data (Figure 1). In fact, if we remove the two highest values (0.033 and 0.016 h^{-1}), both of which were measured on the same day, there does not appear to be a systematic change at all. The shortness of the solar day and the low average rate constants may also contribute to the lack of detectable diurnal variation in midwinter. This marked difference between summer and winter measurements leads to a discussion of seasonal trends.

SEASONAL VARIATIONS

Seasonal or annual trends in the rate of atmospheric SO_2 oxidation have been examined using model calculations and field measurements. Altshuller (1979), using model estimates of "clean" tropospheric HO , HO_2 , and CH_3O_2 radical concentrations, calculated the seasonal dependence of the homogeneous SO_2 oxidation rate. The bulk (70-80%) of the oxidation was attributable to the HO radical whose concentration varied with solar intensity. The noontime rate at 35°N latitude was predicted to increase by approximately a factor of five between January and August.

Meagher et al. (1983) have used data collected during eight plume studies at four coal-fired power plants to demonstrate a similar annual trend. The data were collected during the morning hours at power plants

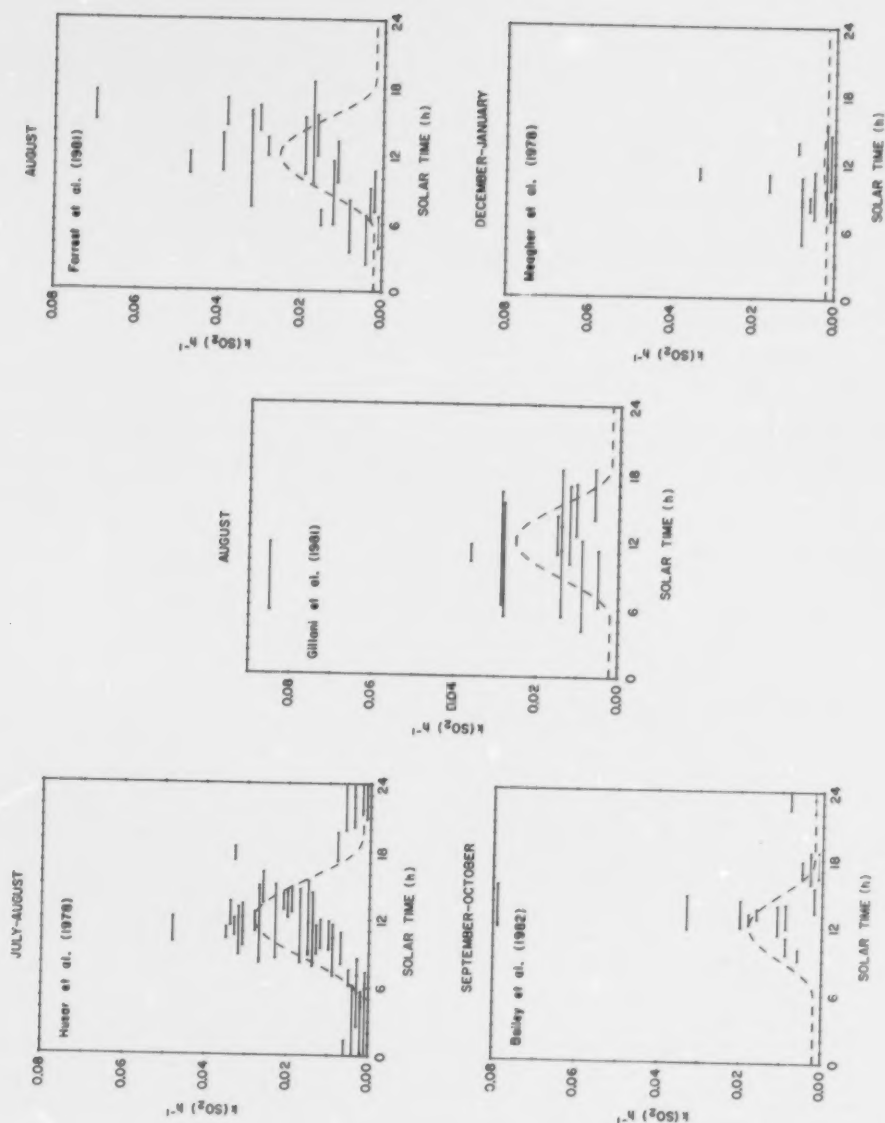


Figure 1. The rate constant for the oxidation of SO_2 to SO_4^{2-} in the atmosphere as a function of time of day (solar). The symbols (*) and connecting bar indicate the period between plume release and measurement. For purposes of consistency, only data collected after one hour or more of drift have been included. The dashed lines denote model estimates for mid-date of study period.

in the TVA system, and were averaged for each study. Because of the similarities in measurement methods and location, the authors believed that these data provided a consistent set of observations with a minimal variation in non-meteorological parameters. The average rate constants calculated varied from a winter low of $1.5 \times 10^{-3} \text{ h}^{-1}$ to a summer high of $1.3 \times 10^{-2} \text{ h}^{-1}$ --a variation similar to that predicted by Altshuller (1979).

MODEL DESCRIPTION

Conceptual Development

An alternative parameterization scheme for estimating the atmospheric SO_2 oxidation rate is presented here. It is intended that this technique complement those described above and other more complex kinetic schemes and be used when the amount of reliable input data is limited.

A model was developed that is based loosely on the diurnal and annual variation in clear-sky, solar intensity. The basic assumption is that the rate constant can be separated into a constant value and a component that is allowed to vary diurnally and annually. The rate constant for any particular time of day and any day of the year can be estimated using the following equation:

$$k(t,i) = k_o + k_{\max} \cdot f_A(i) \cdot f_D(t) \quad (\text{III})$$

where

$k(t,i)$ $\equiv$ the diurnally and annually varying rate constant

t $\equiv$ time of day (solar)

i $\equiv$ Julian date

k_o $\equiv$ the time invariant component of the rate constant

$k_{\max}$ $\equiv$ the maximum value the time variant portion of the rate constant may attain

$f_A(i)$ $\equiv$ a function describing the annual variations in the daily, time variant maximum

$f_D(t)$ $\equiv$ a function describing the diurnal change in the time variant portion of the rate constant

The average nighttime rate constants from the summer diurnal studies cited above were similar to the average winter rate constant (0.002 h^{-1}) reported by Meagher et al. (1978). Thus, it was reasoned that there was a mechanism (possibly heterogeneous) operative which converted SO_2 to SO_4^{2-} and was relatively unaffected by changes in temperature and solar intensity, the remaining variables presumably being averaged out. Thus, k_o was set to 0.002 h^{-1} at the outset. Cosine functions were used to represent the annual and diurnal modifying functions, $f_A(i)$ and $f_D(t)$.

These functions were chosen to approximate the variation in solar intensity that is believed to be the dominant influence in gas phase SO_2 conversion. The period of the diurnal cycle was adjusted to correspond to the solar day using the equation for day length (T_d) given by Duffie and Beckman (1974):

$$T_d = 0.1333 \cos^{-1} (-\tan \phi \tan \delta) \quad (\text{IV})$$

where

ϕ = latitude (degrees - north positive)

δ = declination - degrees (i.e., the angle of the sun at solar noon with respect to the plane of the equator)

The declination can be approximated using the equation of Cooper (1969):

$$\delta = 23.45 \sin 360 \left[\frac{284 + i}{365} \right] \quad (\text{V})$$

where i is the Julian date.

Data Base

The data used to establish the remaining parameters needed for the model represent the results from 12 field studies. The field studies and their locations are listed in Table 1. Because all the measurements were made in the same region of the country, they should provide the best opportunity for a fit to a simple function such as the one proposed. Best fits were obtained for the diurnal data first. These fits were then used to estimate midmorning rate values that were, in turn, combined with the seasonal data (Meagher et al., 1983) to fit the seasonal function.

Diurnal Function $f_D(t)$

Although it has been proposed (Husar et al., 1978) that the rate constant maximum should lag behind the solar maximum, there appears to be no such trend evident in the diurnal data (Figure 1). Thus, for purposes of the model, the maximum rate was assumed to correspond to solar noon. The rate constant expression can be generalized for a specific Julian date (i) in the following form that is valid for the daylight hours.

TABLE 1. MEASUREMENTS OF THE ATMOSPHERIC SO₂ OXIDATION RATE
CONSTANT IN THE PLUMES FROM COAL-FIRED POWER PLANTS

Reference	Experimental Dates	Plant/Location
Husar et al. (1978)	August 1974, July 1976	Labadie/MO
Forrest et al. (1981)	August 1978	Cumberland/TN
Gillani et al. (1981)	August 1978	Cumberland/TN
Bailey et al. (1982)	September-October 1979	Widows Creek/AL
Meagher et al. (1978)	December 1975- January 1976	Cumberland/TN
Meagher et al. (1981a)	August-September 1977	Cumberland/TN
Meagher et al. (1981b)	May-June 1978	Colbert/AL
Meagher et al. (1981b)	August 1978	Widows Creek/AL
Meagher et al. (1982a)	June 1978	Paradise/TN
Meagher et al. (1982b)	September 1976	Cumberland/TN
Meagher et al. (1982b)	May 1977	Colbert/AL

$$k(t)_i = k_o + \frac{k(i)_{\max}}{2} \left[\cos \frac{2\pi(t-12)}{T_d} + 1 \right] \quad (VI)$$

$$= k_o + k(i)_{\max} \cdot f_D(t)$$

where

$k(i)_{\max} \equiv$ rate constant at solar noon for day i

and

$$k(t)_i = k_o \begin{cases} \text{if } t < 12 - \frac{1}{2} T_d \\ \text{or} \\ \text{if } t > 12 + \frac{1}{2} T_d \end{cases} \quad (VII)$$

The reported rate constants are average values, averaged over the period from release to measurement. For a time dependent rate constant, the average value ($\bar{k}$) during any period of the solar day ($t_1 \rightarrow t_2$) is given by

$$\bar{k} = \frac{\int_{t_1}^{t_2} k(t)_i dt}{t_2 - t_1} \quad (VIII)$$

Substituting the proposed functionality for $k(t)_i$ and integrating

$$\bar{k} = k_o + \frac{T_d \cdot k(i)_{\max}}{4\pi(t_2-t_1)} \left[\sin \frac{2\pi}{T_d} (t_2-12) - \sin \frac{2\pi}{T_d} (t_1-12) + \frac{2\pi}{T_d} (t_2-t_1)^2 \right] \quad (IX)$$

which is an equation of the form

$$\bar{k} = k_o + k(i)_{\max} \cdot g(t_1, t_2) \quad (X)$$

Values for $g(t_1, t_2)$ have been calculated for each of the plume measurements (Husar et al., 1978; Forrest et al., 1981; Gillani et al., 1981; Bailey et al., 1982; Meagher et al., 1978). Estimates of $k(i)$ have been obtained for each study by plotting $\bar{k}$ against $g(t_1, t_2)$ and $k(i)_{\max}$ per forming a least squares fit while forcing the line through 0.002 h^{-1} at $g(t_1, t_2) = 0$. The objective of the model is to reproduce average situations rather than events, thus a single outlier has been removed from each data set to prevent it from unduly biasing the fit. The correlation coefficient (r) provides an indication of the quality of the fit obtained with the cosine function. The results of the fits are given in Table 2.

TABLE 2. COSINE FIT TO DIURNAL DATA^a

Reference	Study midpoint Julian date	$k(i)_{\max}$ h^{-1}	Correlation coefficient r
Husar et al., 1978	207	0.0229	0.83
Forrest et al., 1981	235	0.0305	0.64
Gillani et al., 1981	235	0.0234	0.57
Bailey et al., 1982	271	0.0145	0.68
Meagher et al., 1978	362	0.0031	0.25

^aOne outlier has been excluded from each data set.

A good correlation was obtained between $\bar{k}$ as measured and the $g(t_1, t_2)$'s calculated from the cosine function for all data except the winter measurements of Meagher et al. (1978). The low correlation coefficient for the winter data indicates a lack of significant diurnal variation as mentioned above. The natural and experimental variability in the data is amplified at the lower rates, which undoubtedly also contributes to the low correlation.

Annual Function $f_A(i)$

The annual variation in the daily maximum rate constant ($k(i)_{\max}$) was determined from the expression

$$\begin{aligned} k(i)_{\max} &= \frac{k_{\max}}{2} \left[\cos \frac{2\pi(i-i_{\max})}{365} + 1 \right] \\ &= k_{\max} \cdot f_A(i) \end{aligned} \quad (XI)$$

where

$i_{\max} \equiv$ Julian date on which $k_{\max}$ occurs.

The seasonal trend in the SO_2 rate constant as described by Meagher et al. (1983) is based on morning rate measurements. The mean solar time for each of these average rate constants is 8.4 ± 0.9 a.m. The rate constant, corresponding to the same solar time, was calculated for each of the five diurnal studies using equation VI and the $k(i)_{\max}$ values from Table 2. The combined data sets are shown in Figure 2.

The annual maximum time variant rate constant at solar noon ($k_{\max}$) and the date of that maximum ($i_{\max}$) were adjusted to obtain the best fit to the data in Figure 2 using equations VI and XI. The best fit was obtained for

$$\begin{aligned} k_{\max} &= 0.0265 \text{ h}^{-1} \\ i_{\max} &= 192.5 \end{aligned}$$

Thus the maximum noon rate coefficient of 0.0285 h^{-1} is predicted for mid-July, 20 days after the summer solstice. This is consistent with the general observation that ozone levels tend to maximize in mid-summer rather than in June when the solar intensity is greatest. Ozone is an indicator of photochemical activity and, therefore, presumably of SO_2 reactivity.

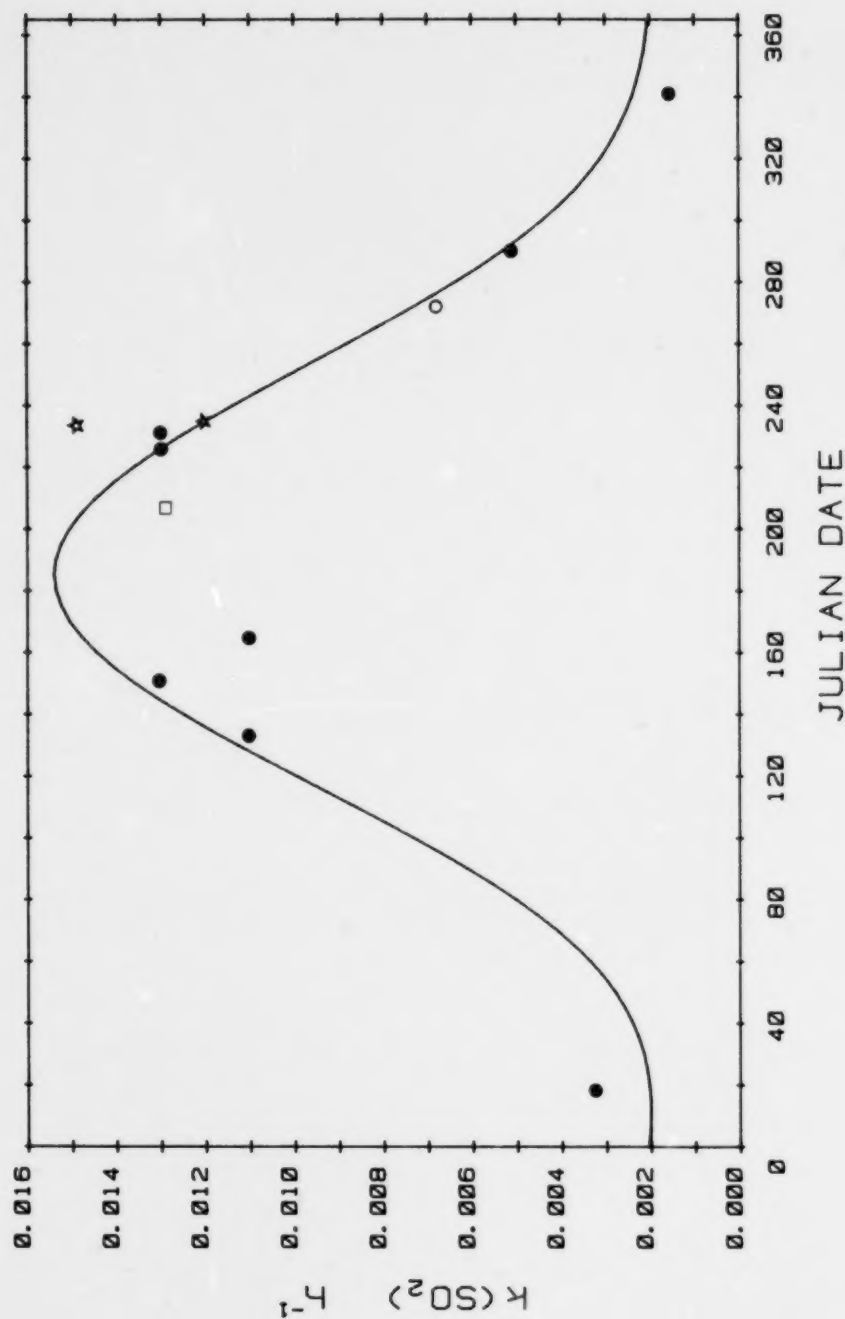


Figure 2. $k(\text{SO}_2)$ versus Julian date--combined data set. (●) Data of Meagher et al. (1983). The remaining points have been estimated for 8.4 AM (solar) using the data of Husar et al. (1978) (□); Forrest et al. (1981) (☆); Gillani et al. (1981) (★); and Bailey et al. (1932) (○). Solid line denotes fit to data using empirical model calculation for 8.4 AM (solar) and latitude 36.5°N (mean latitude of measurements).

Model Results

A combination of the diurnal and seasonal functions provides the following equation for the pseudo first order rate constant.

$$k(i,t,T_d) = 0.002 + 0.006625 \left[\cos \frac{2\pi(i-192.5)}{365} + 1 \right] \cdot \left[\cos \frac{2\pi(t-12)}{T_d} + 1 \right] \quad (\text{XII})$$

where $k(i,t,T_d)$ is in units of h^{-1} .

The model predicted time-of-day variation in k is shown, for each of the diurnal studies, in Figure 1. A comparison of measured and calculated average rate constants ($\bar{k}$'s) for the 103 individual measurements (excluding the 5 outliers) from these same studies is presented in Figure 3. A linear regression analysis indicates that this simple empirical model accounts for 56 percent of the observed variation.

The daily maximum and 24-hour average rate constants predicted by equation XII are shown in Figure 4. The values predicted by the empirical model are significantly higher than the estimates of Altshuller's free radical model (Figure 4). Thus if, as is generally believed, the dry atmosphere conversion is dominated by free radical processes, the concentrations of these radicals must be higher in the rural southeast and midwest than in the background air simulated in Altshuller's model. This may be a manifestation of higher hydrocarbon levels in these areas relative to global background.

LIMITATIONS

The simple model presented here utilized a consistent data set from multiple field studies conducted in each of the four seasons to optimize its parameters. The model is intended to represent the average situation. It should not be expected to exhibit significant skill in reproducing individual events. It is simply a representation of past experience and will be correct only in the sense that the experiences were representative.

Virtually all the field measurements of SO_2 oxidation have been made in rural areas; the Labadie study being a possible exception. Experience has shown that urban areas, with their local emissions, can significantly alter the observed rate constant (Luria et al., 1983). Thus, the extrapolation of these data to the urban environment must be done with caution.

The model is based on measurements made under "dry" conditions, i.e., in the absence of interaction with clouds or precipitation. It should not be expected to accurately reproduce measurements performed when aqueous phase chemistry plays a significant role in sulfate formation.

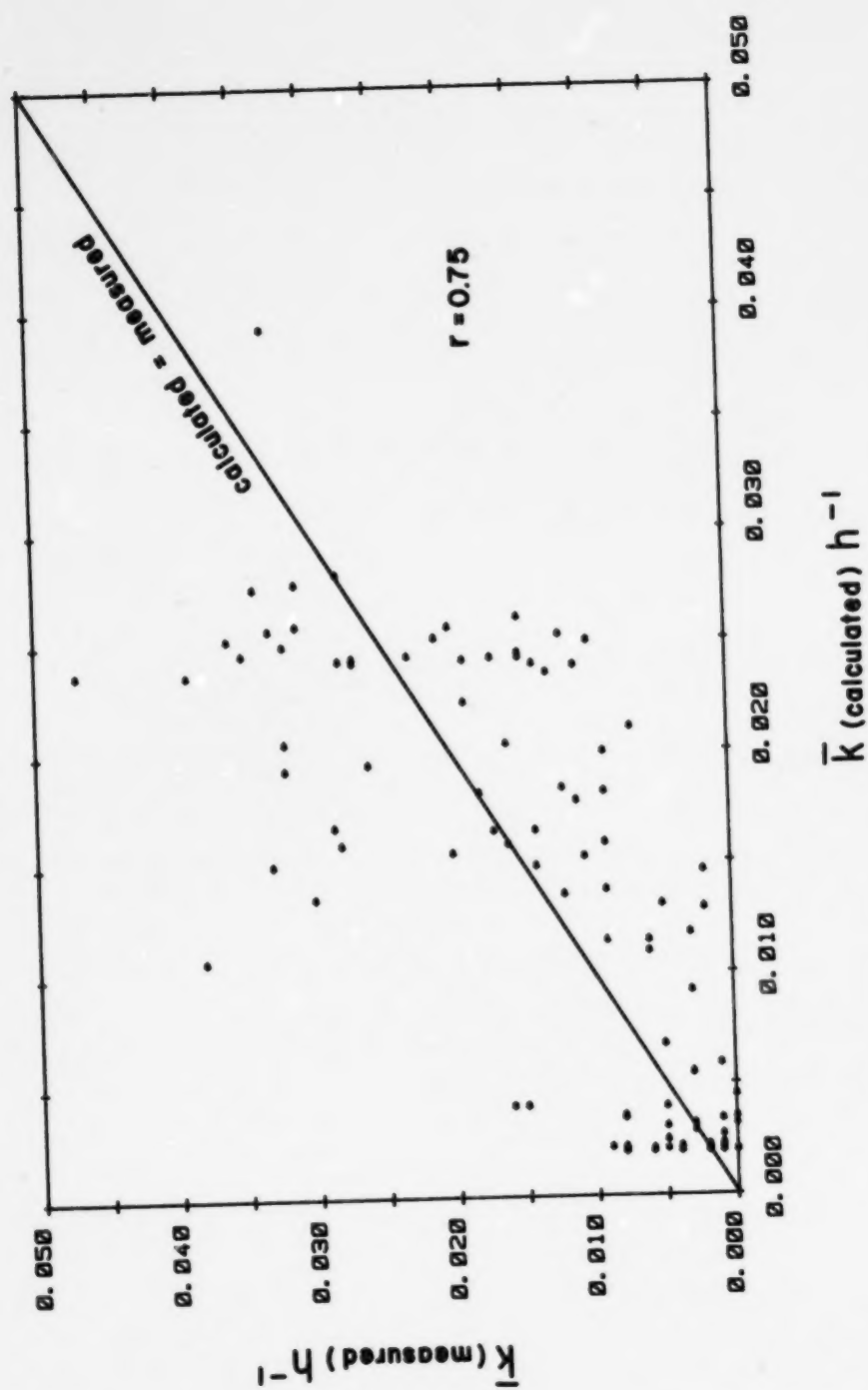


Figure 3. Comparison of measured and calculated average rate constants using data from Figure 1.

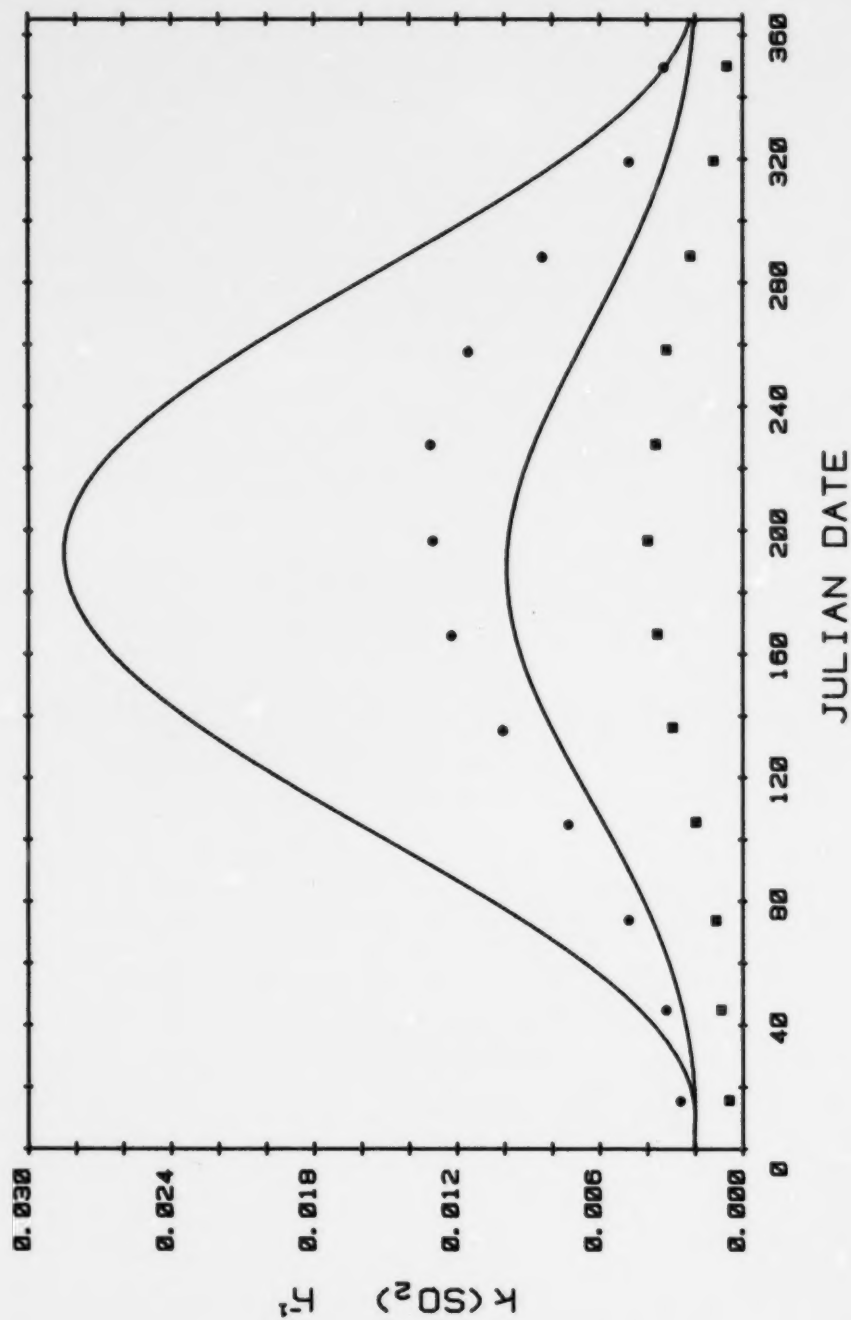


Figure 4. Model predictions of daily maximum (upper curve) and diurnal average (lower curve) rate constants as a function of Julian date. Also shown are "clean" troposphere calculations of Altshuller (1979) for 35°N latitude. (●) designate daily maximum values while (■) indicate diurnal averages.

KINETIC MODELS

Many of the limitations inherent in empirical models can be avoided through the use of detailed kinetic schemes. As the name implies, this approach presupposes an understanding of the mechanism(s) that is(are) operative and requires rate data for the elementary and composite reactions that make up these mechanisms.

MECHANISM OF GAS PHASE SO₂ OXIDATION

Calvert and Stockwell (1984) have recently reviewed the available data on gas phase SO₂ oxidation in the atmosphere. These authors concluded that hydroxyl radical (HO) addition was the single most important reaction in the oxidation processes. Theoretical estimates and a few measurements of HO concentrations in rural atmospheres would support SO₂ oxidation rates in agreement with those measured in plumes.

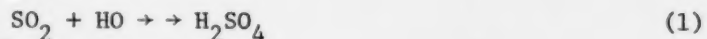
At the higher hydrocarbon/NO_x ratios and pollutant concentrations found in urban areas, a second mechanism contributes significantly to SO₂ oxidation. This mechanism is, at present, poorly understood but involves the products of the ozone-alkene reaction. Smog chamber experiments (Miller, 1978; Olszyna and Meagher, 1983) have demonstrated the conversion from an hydroxyl dominated oxidation to one involving O₃-alkene products with increasing alkene concentrations.

A model that is to be used for rural or global assessments could probably ignore the contribution of the O₃-alkene mechanism without significantly affecting the predictions of atmospheric SO₄²⁻ production. However, to adequately simulate SO₄²⁻ formation in an urban environment, both mechanisms must be considered.

Data collected during a series of experiments conducted in the TVA smog chamber (described in Appendix A) were used to evaluate the various kinetic schemes that have been proposed to explain atmospheric SO₂ oxidation. These experiments were conducted at low pollutant concentrations to enhance the effect of the sulfur chemistry and to more realistically simulate atmospheric conditions.

HO + SO₂

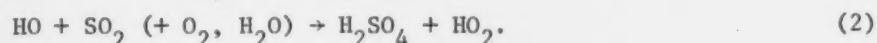
Most atmospheric modelers have assumed that SO₂ is an HO chain terminator and have thus summarized the overall oxidation by the chemical equation:



(e.g., Rodhe et al., 1981; Atkinson et al., 1982; Meagher and Luria, 1982c; and others). If SO₂ is assumed to be an HO chain terminator, then model calculation predicts a high degree of non-linearity in the

relationship between SO_2 emission levels and ambient SO_4^{2-} concentrations (Meagher and Luria, 1982c). In addition, the assumption of chain termination led these authors to suggest that a reduction in SO_2 concentration could enhance NO_3^- production. On the other hand, if $\text{HO}^\bullet$ radicals are regenerated, then a more linear relationship between SO_2 concentrations and SO_4^{2-} formation would be expected with little or no effect on NO_3^- formation.

Recently, Stockwell and Calvert (1983) studied the $\text{HO}-\text{SO}_2$ reaction mechanism by photolyzing mixtures of HONO in the presence of SO_2 , NO , NO_2 , H_2O , and CO . By extrapolating their data to atmospheric conditions, they concluded that SO_2 is not an HO chain terminator. On the basis of their data, they suggested that the overall oxidation process can be summarized in one equation:



Although this reaction is thermochemically favorable by 53 kcal mole⁻¹, Stockwell and Calvert were unable to prove the elementary reactions that result in this overall equation.

A series of smog chamber experiments has been performed at TVA to further evaluate the various mechanistic options for atmospheric SO_2 oxidation. In these experiments, the efficiency of SO_2 as an HO chain terminator was evaluated by determining the effect of added SO_2 on steady-state HO levels.

Experimental conditions for the various chamber experiments are presented in Table 3. Chamber experiments were performed at constant initial NO and hydrocarbon concentrations with variable amounts of added SO_2 (0 to 6.4 ppm). Experiments were conducted at low and moderate humidity levels (~5% and 40% relative humidity, respectively, at 25°C). The major reactive hydrocarbon used in this study was propene; in addition, n-butane was also added to all experiments to allow in situ monitoring of HO radical levels. The hydroxyl radical concentration estimated from the loss of propene, corrected for its reaction with O_3 and dilution, was in good agreement ($\pm 25\%$) with the HO concentration estimated from the loss of butane.

The overall effect of SO_2 on the conversion of NO to NO_2 and on the formation of O_3 are shown in Figure 5, for the low H_2O content, and Figure 6, for higher H_2O content. These figures reveal that, under both "dry" and "wet" conditions, SO_2 was found to slightly accelerate the conversion of NO to NO_2 and to increase the O_3 peak concentration. On the other hand, as SO_2 concentration increased, the HO steady state concentration (as determined from the loss rate of C_3H_6 and C_4H_{10}) was found to decrease. The observed changes were well beyond the experimental uncertainty. Hydroxyl radical concentrations averaged over the entire irradiation period (4 hours) and calculated independently from the C_3H_6 and C_4H_{10} loss rates are presented in Table 4. The time dependent HO concentrations for the experiments with 0, 3.07, and 6.38 ppm of added SO_2 are shown in Figure 7.

TABLE 3. SUMMARY OF INITIAL CONDITIONS AND EXPERIMENTAL PARAMETERS

Initial concentrations (ppm)	CH82-334	CH82-340	CH82-337	CH82-307	CH82-343	CH83-222	CH83-165	CH83-161	CH83-216	CH83-244
SO ₂	.0	.147	1.81	4.51	5.87	.0	0.195	1.51	3.07	6.38
NO	.053	.052	.053	.055	.051	.051	.053	.052	.052	.056
NO _x	.055	.053	.054	.056	.052	.052	.054	.053	.053	.057
C ₃ H ₆	.109	.107	.110	.107	.110	.108	.107	.109	.109	.101
C ₄ H ₁₀	.058	.057	.060	.056	.060	.059	.060	.059	.058	.057
CO	.4	.2	.1	.2	.3	.7	.2	.7	.4	.9
H ₂ O	1,500	1,400	1,650	1,500	1,250	14,500	14,500	14,700	14,200	14,000
Experimental parameters										
k _d ^a (h ⁻¹)	.165	.159	.164	.165	.165	.163	.158	.156	.164	.164
J{NO ₂ } ^b (min ⁻¹)	0.390	0.391	0.384	0.415	0.386	.172	.177	.178	.174	.170
Temperature (°C)	27	21	31	23	22	37	35	34	37	39

^aDilution rate coefficient.^bNO₂ photolytic rate coefficient.

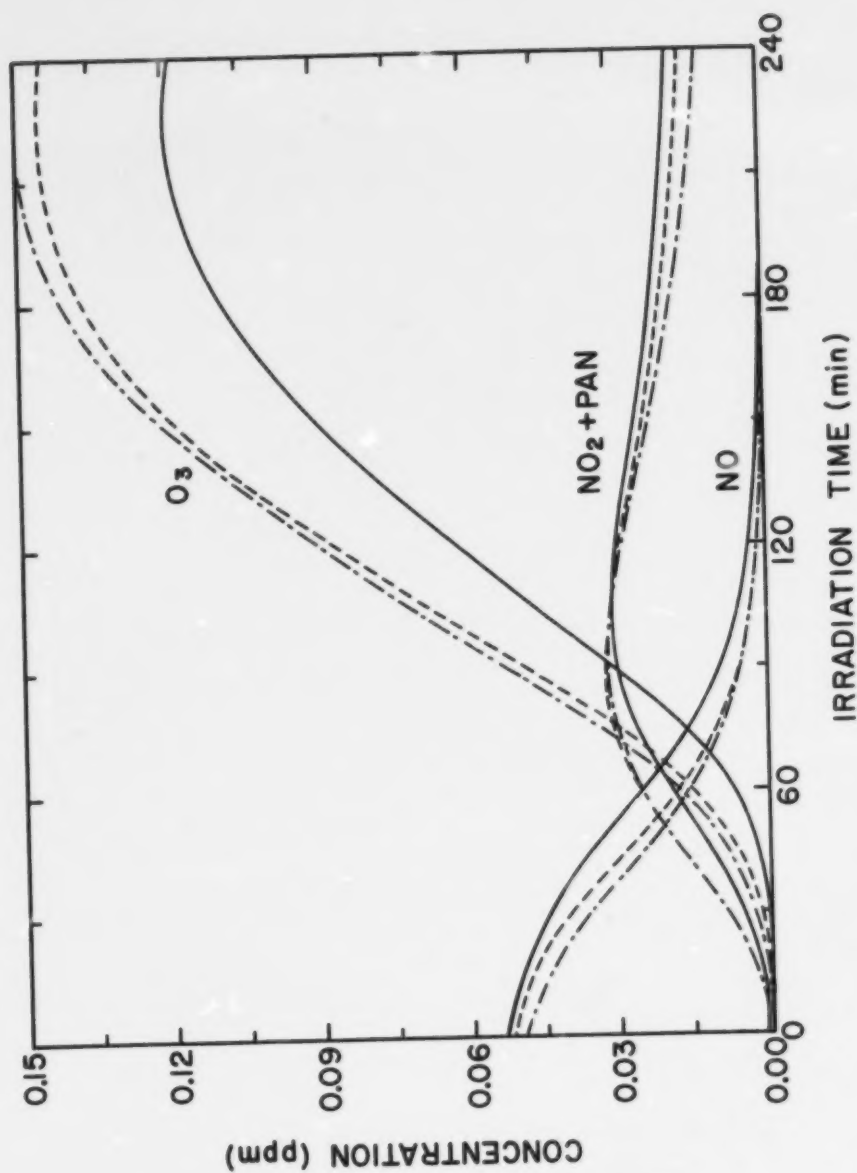


Figure 5. The effect of SO_2 on the rate of NO loss and on the rates of NO_2 and O_3 formation in smog chamber experiments with low H_2O content; SO_2 concentrations 0 (—), 4.51 (---), and 5.37 (-·-·-) ppm.

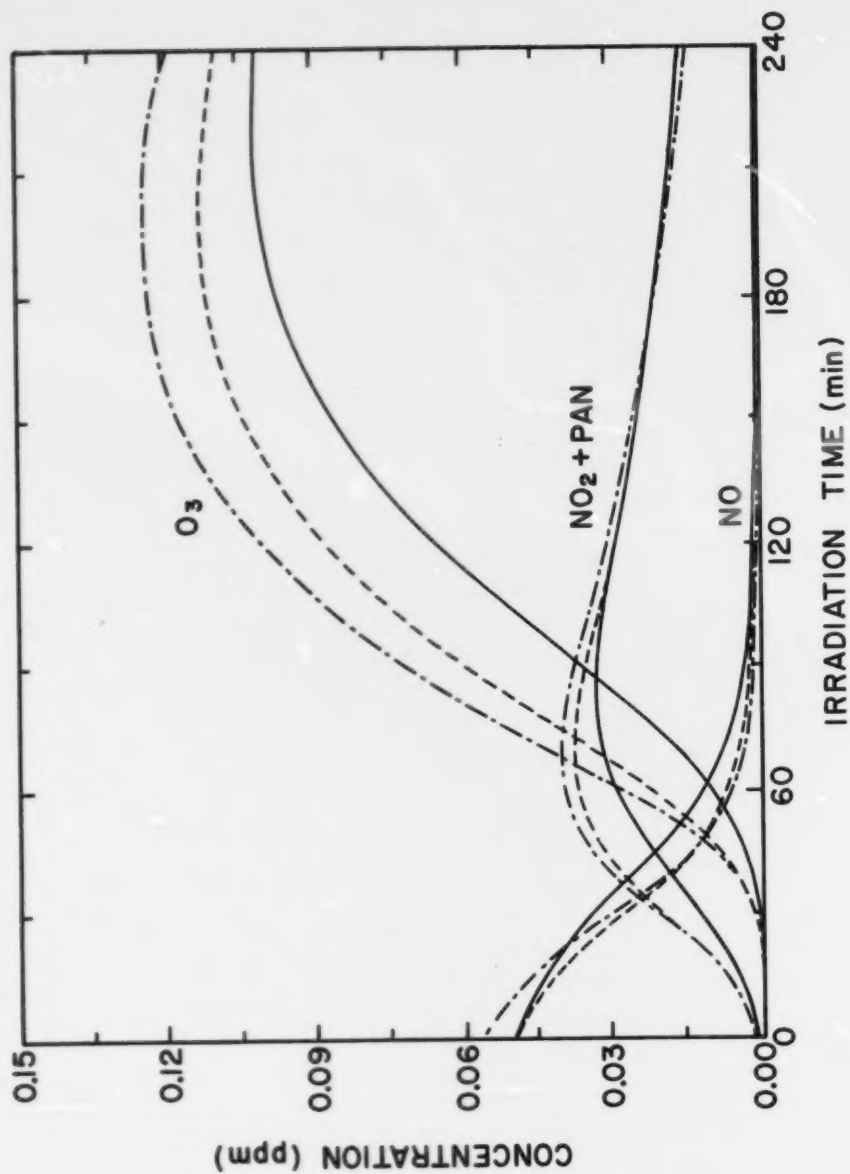


Figure 6. The effect of SO₂ on the rate of NO loss and on the rates of NO₂ and O₃ formation in smog chamber experiments with moderate H₂O content; SO₂ concentrations 0 (—), 3.07 (---), and 6.38 (— · —) ppm.

TABLE 4. AVERAGE [HO] CALCULATED FROM C_3H_6 LOSS RATE
 $([HO]_p)$ AND FROM C_4H_{10} LOSS RATE $([HO]_b)$

Experiment code	$[SO_2]_o$ (ppm)	$[HO]_p$ ($\times 10^7$ ppm)	$[HO]_b$ ($\times 10^7$ ppm)
CH82334	0.0	2.4 ± 0.7	2.2 ± 0.7
CH82340	0.147	2.3 ± 1.1	1.9 ± 0.8
CH82337	1.81	2.1 ± 0.6	1.9 ± 0.7
CH82307	4.51	1.6 ± 0.5	1.5 ± 0.5
CH82343	5.86	1.3 ± 0.4	1.3 ± 0.6
CH83222	0.0	2.4 ± 0.4	2.1 ± 0.4
CH83165	0.195	2.4 ± 0.2	2.0 ± 0.4
CH83161	1.51	2.1 ± 0.3	1.8 ± 0.5
CH83216	3.07	1.7 ± 0.3	1.6 ± 0.8
CH83244	6.38	1.4 ± 0.2	1.1 ± 0.6

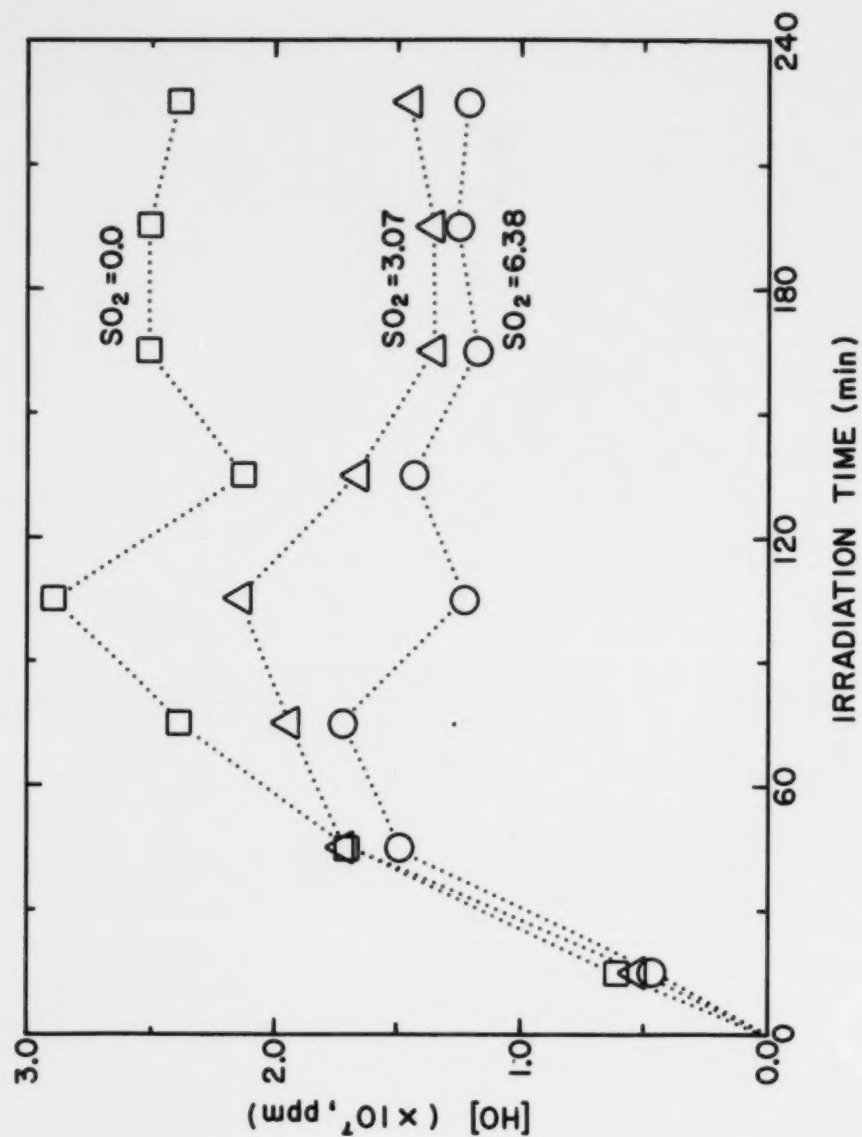


Figure 7. Steady-state concentrations of HO radicals calculated from hydrocarbon loss rate for experiments CH83222 (□), CH83216 (△), and CH83244 (○).

A comparison between the "wet" and "dry" experiments reconfirms the previous observation (e.g., Sakamaki et al., 1980) that water vapor enhances the photochemical activity in these systems. In these experiments, it was desirable to maintain the same HO levels in both "wet" and "dry" experiments. In order to achieve this, light intensity was reduced in the "wet" experiments.

The hydroxyl radical concentrations estimated for each experiment were used to calculate the rate of SO_2 to SO_4^{2-} formation, using the rate coefficient recommended by Atkinson and Lloyd (1984) for the HO- SO_2 reaction ($1.39 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$, at 305°K and 1 atm). These values were compared with the average SO_2 to SO_4^{2-} conversion rates that were determined by monitoring the rate of aerosol volume increase, utilizing the method described previously (Olszyna et al., 1983). The excellent agreement, as shown in Table 5, between calculated and measured SO_4^{2-} formation rates indicates that, under the conditions employed, HO addition to SO_2 can account for all the measured SO_4^{2-} .

Model Development

Computer simulations were performed to evaluate the details of the mechanism involved in the oxidation of SO_2 to SO_4^{2-} . A modified version of the photochemical scheme proposed by Atkinson et al. (1982) was tested with input data from SO_2 -free experiments (see Appendix B). As is the case in all smog chamber models (e.g., Carter et al., 1982), a supplementary source of HO radicals has been introduced to obtain acceptable agreement between calculated and observed concentrations. Although the exact nature of this radical source has not been determined, it has been suggested that this effect is due, at least in part, to the photolysis of nitrous acid ($\text{HONO} \rightarrow \text{HO} + \text{NO}$) which may be formed in a heterogeneous wall reaction (e.g., Whitten et al., 1980; Carter et al., 1982). In this study, the unknown source of HO radicals needed to fit the data was $(3.5 \pm 1.0) \times 10^{-5} \text{ ppm min}^{-1}$, which is approximately 10% of the levels previously employed by Atkinson et al., (1982) in their smog chamber modeling. This source contributes approximately 5 percent to the homogeneous HO production in the chamber and, therefore, permits these experiments to be more sensitive to changes in chemical rather than external parameters. The fit between the experimental data and the model calculation for the SO_2 -free experiment is shown in Figure 8.

Two extreme mechanistic approaches have been used to explain sulfuric acid production following HO addition to SO_2 . The results of the TVA chamber experiments provide an opportunity to determine whether this reaction results in termination of the HO chain (Rodhe et al., 1981; Atkinson et al., 1982; Meagher and Luria, 1982c) or propagation through the production of HO_2 (Cox, 1974; Stockwell and Calvert, 1983).

The first mechanism to be tested was the simple HO chain termination as expressed in reaction (1). The reduction in HO steady-state concentration predicted by this mechanism severely inhibited photochemical reactivity that resulted in an extreme underestimation of the formation

TABLE 5. AVERAGE SO_2 TO SO_4^{2-} CONVERSION RATE COEFFICIENT
CALCULATED FROM THE HO STEADY-STATE CONCENTRATION (k_{HO})
AND FROM THE RATE OF INCREASE IN AEROSOL VOLUME (k_{VOL})

Experiment code	$[\text{SO}_2]_0$ (ppm)	k_{HO} ($\times 10^{-2} \text{ h}^{-1}$)	k_{VOL} ($\times 10^{-2} \text{ h}^{-1}$)
CH82334	0.0	NA	-
CH82340	0.15	1.9 ± 0.9	1.9 ± 0.8
CH82337	1.81	1.7 ± 0.6	1.9 ± 0.5
CH82307	4.51	1.4 ± 0.4	1.4 ± 0.3
CH82343	5.87	1.2 ± 0.5	1.2 ± 0.3
CH83222	0.0	NA	-
CH83165	0.195	1.8 ± 0.2	1.9 ± 0.9
CH83161	1.51	1.6 ± 0.3	1.4 ± 1.0
CH83216	3.07	1.3 ± 0.5	1.4 ± 0.5
CH83244	6.38	1.0 ± 0.3	0.8 ± 0.5

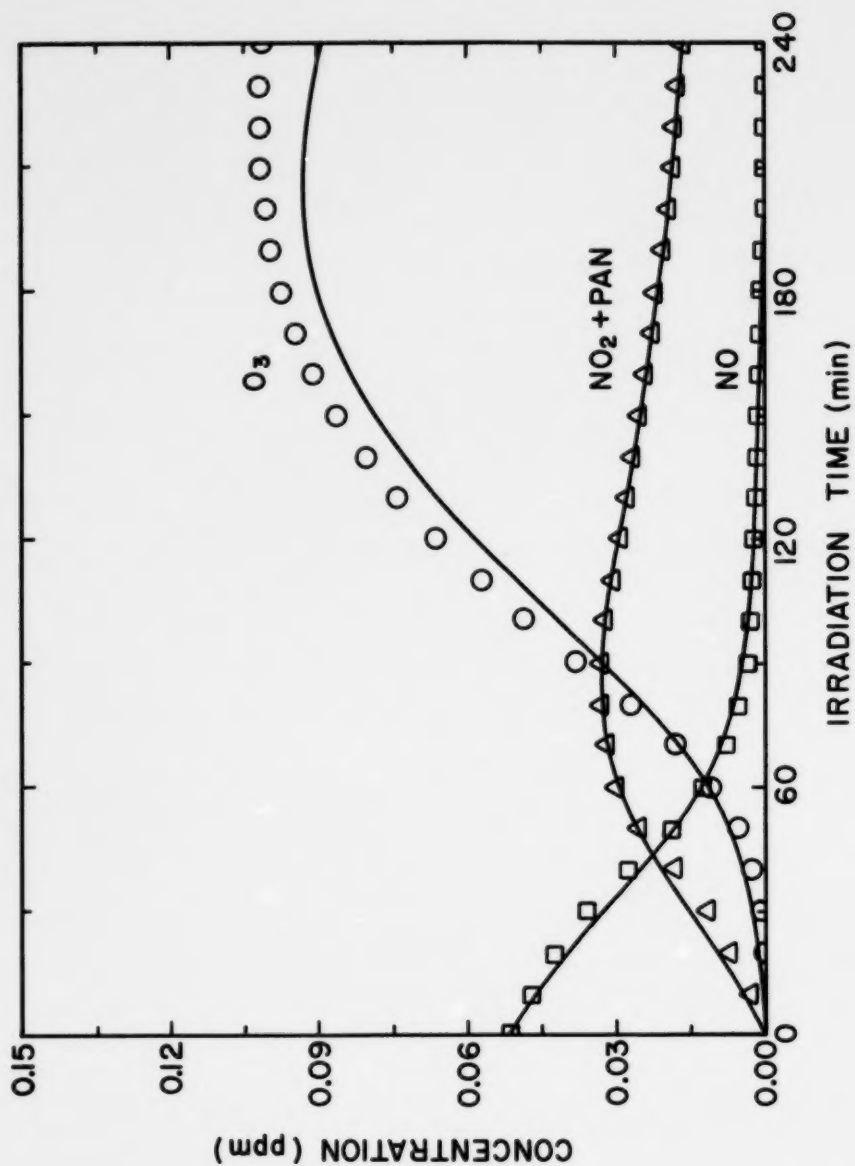
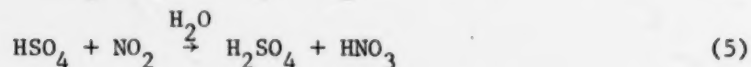
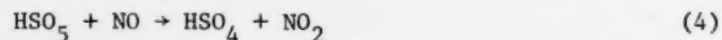
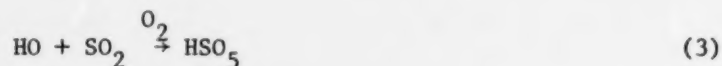


Figure 8. Comparison between experimental and model calculated NO ($\square$), NO₂ + PAN (Δ), and O₃ (O) time-dependent concentrations for the SO₂-free experiment (CH83222).

of secondary products. Model predictions using this scheme displayed very slow NO to NO₂ conversion that resulted in an unrealistic O₃ production as can be seen in Figure 9 for the experiment with 1.3 ppm SO₂. The sensitivity of these photochemical systems to the addition of SO₂ is determined by the rate of the HO-SO₂ reaction relative to other HO radical reactions. In this study, reaction with SO₂ represents a significant sink for HO radicals (~35% for the experiment with 1.5 ppm SO₂). Atkinson et al. (1982) were able to use the termination mechanism successfully to model the experiments of Miller (1978) because reaction (1) represented an insignificant fraction of the total HO loss (less than 2%) in those experiments.

A modified version of the simple termination mechanism has been suggested by Seigneur (1982).



This mechanism also severely underestimates NO → NO₂ conversion and the O₃ maximum due to the lack of an HO radical regeneration step. Moreover, if reaction 5 were the only route to H₂SO₄, then HNO₃ would always be greater than H₂SO₄ because HNO₃ can also be produced by HO addition to NO₂, and the amount of H₂SO₄ formed would be limited by available NO₂. Because H₂SO₄ was produced in excess of the initial NO in several experiments, reaction 5 cannot be the only one producing H₂SO₄.

A better agreement between experimental data and model fit was obtained when reaction (1) was substituted by a simplified version of reaction (2)



proposed by Calvert and Stockwell (1983) for the free atmosphere. The comparison between the model predicted and the experimentally measured NO, NO₂, and O₃ is shown in Figure 10. This model qualitatively predicts the main chemical changes observed, i.e., accelerated NO to NO₂ conversion, enhanced O₃ formation, and depression of HO steady-state concentration with added SO₂. The experimental data show (Figure 7) and this model predicts that in the early stages of the experiment the HO concentration is insensitive to added SO₂, presumably because HO₂ produced in reaction (6) regenerates HO by reacting with NO. The lack of NO at the latter stages of the experiment inhibits the conversion of HO₂ to HO, thereby significantly reducing the HO steady-state concentration. However, this mechanism overestimates the increase in O₃ formation resulting from the addition of SO₂.

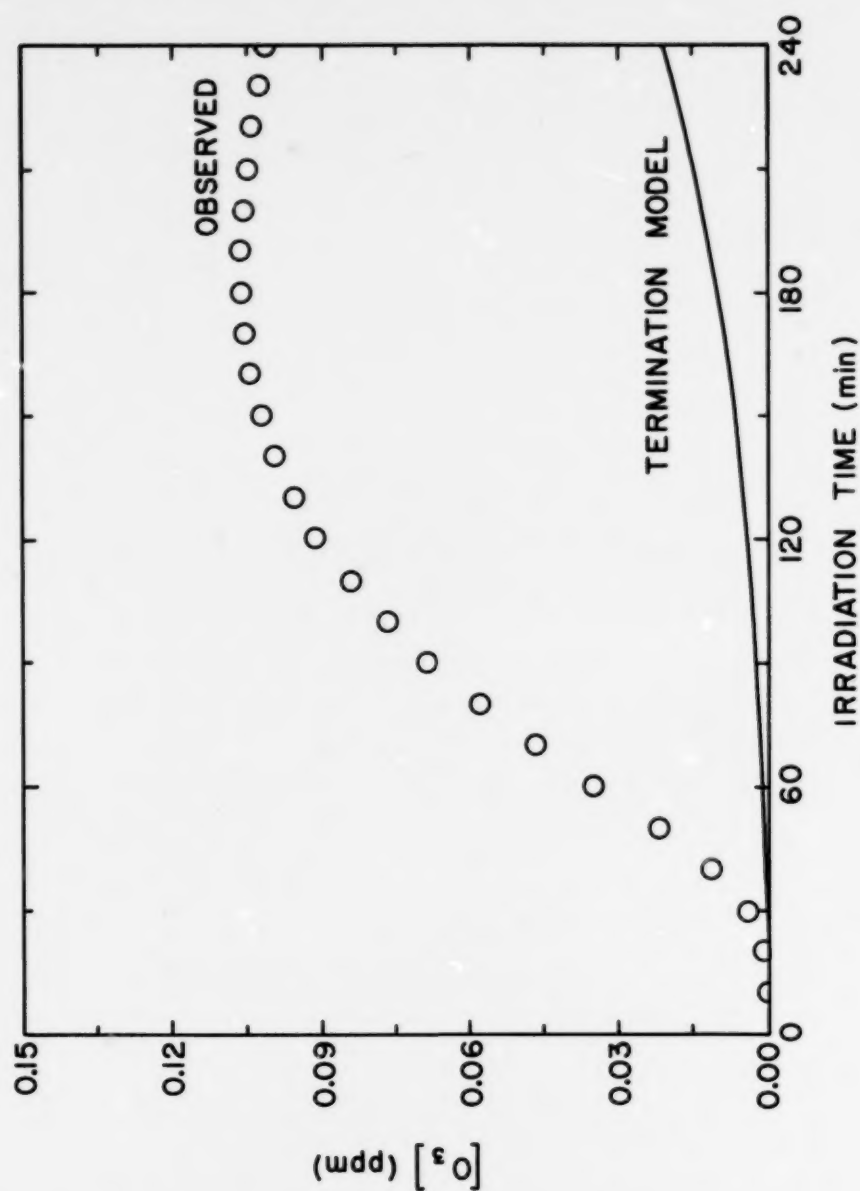


Figure 9. Comparison between model prediction and experimentally observed O_3 time-dependent concentration for the experiment with initial SO_2 concentration of 1.51 ppm (experiment CH83161). The model assumes that the $HO + SO_2$ reaction terminates the chain.

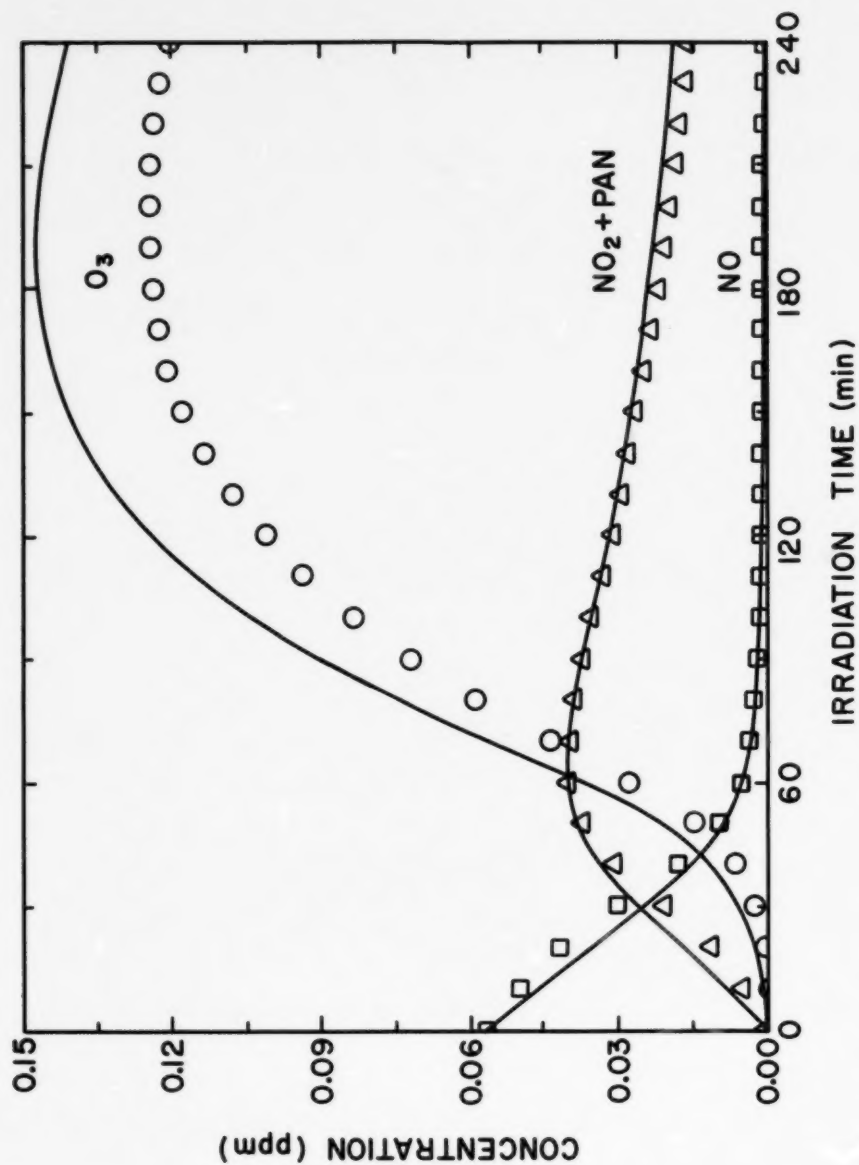
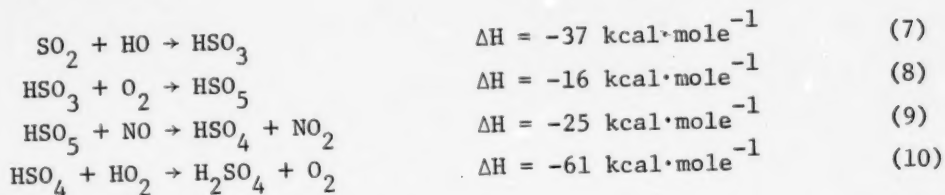


Figure 10. Comparison between model predictions and observed NO ($\square$), NO₂ + PAN (Δ), and O₃ (O) concentration profiles for the experiment with initial SO₂ concentration of 6.38 ppm (experiment CH83244). Model assumes that the HO + SO₂ reaction produces HO₂ at unit efficiency.

It is obvious from the above analyses that the assumption of an HO chain propagation mechanism involving the formation of HO_2 , which is subsequently converted to HO, is by far a better approximation to the experimental data than that provided by termination. Nevertheless, the data suggest that additional HO termination routes are needed.

Previous homogeneous mechanisms describing the oxidation of SO_2 via HO radicals have included HSO_3 , HSO_5 , and HSO_4 free radicals (Calvert et al., 1978; Davis et al., 1979). On the basis of the thermochemical data evaluated by Benson (1978), several reactions, which may occur in this system, were proposed:



To incorporate these reactions in the model, it was assumed that reactions (8) and (9) are very fast (k_8 and k_9 are greater than $10^5 \text{ ppm}^{-1} \text{ min}^{-1}$). The rate coefficient k_{10} was estimated, by comparison with other HO_2 disproportionation reactions, to be in the range of 10^2 - $10^5 \text{ ppm}^{-1} \text{ min}^{-1}$. The addition of these reactions in the model considerably enhanced the fit to the O_3 data in the early stages of the experiment. However, very little improvement was achieved in the prediction of the O_3 maximum.

The model overestimation of the O_3 maximum suggests the presence of additional reaction(s) that consume O_3 or its precursor(s). A simple reaction that satisfies this requirement is:



This reaction is analogous to the $\text{HO} + \text{O}_3$ reaction that plays an important role in smog chemistry. By adjusting the ratios k_6/k_7 and k_{10}/k_{11} , very good agreement between model prediction and experimental data was obtained. The rate coefficients used for the simulations are listed in Table 6. The improved agreement obtained with this mechanism, relative to previous ones, is demonstrated in Figure 11 in which the observed O_3 is compared with the model prediction for the experiments with 0, 3.07, and 6.38 ppm of added SO_2 . Figures 12 and 13 show the agreement for C_3H_6 , C_4H_{10} , NO, and $\text{NO}_2 + \text{PAN}$ for the experiment with the highest SO_2 .

Because this and other research programs are directed toward the development of the capability to predict ambient SO_4^{2-} levels, it is of interest to compare the model prediction of SO_4^{2-} concentration with the observed values. Figure 14 shows the excellent agreement obtained between predicted and observed values. This study also provided a

TABLE 6. LIST OF ESTIMATED RATE COEFFICIENTS USED TO
MODEL SO₂ OXIDATION IN CHAMBER STUDY

Reaction	Rate constant ^a (ppm ⁻¹ min ⁻¹)
HO + SO ₂ (+ H ₂ O, O ₂) → H ₂ SO ₄ + HO ₂	1.37 × 10 ³
HO + SO ₂ → HSO ₃	2.08 × 10 ¹
HSO ₄ + HO ₂ → H ₂ SO ₄ + O ₂	2.5 × 10 ²
HSO ₄ + O ₃ → HSO ₅ + O ₂	1.0 × 10 ¹

^aValue listed is for 305°K and one atmosphere.

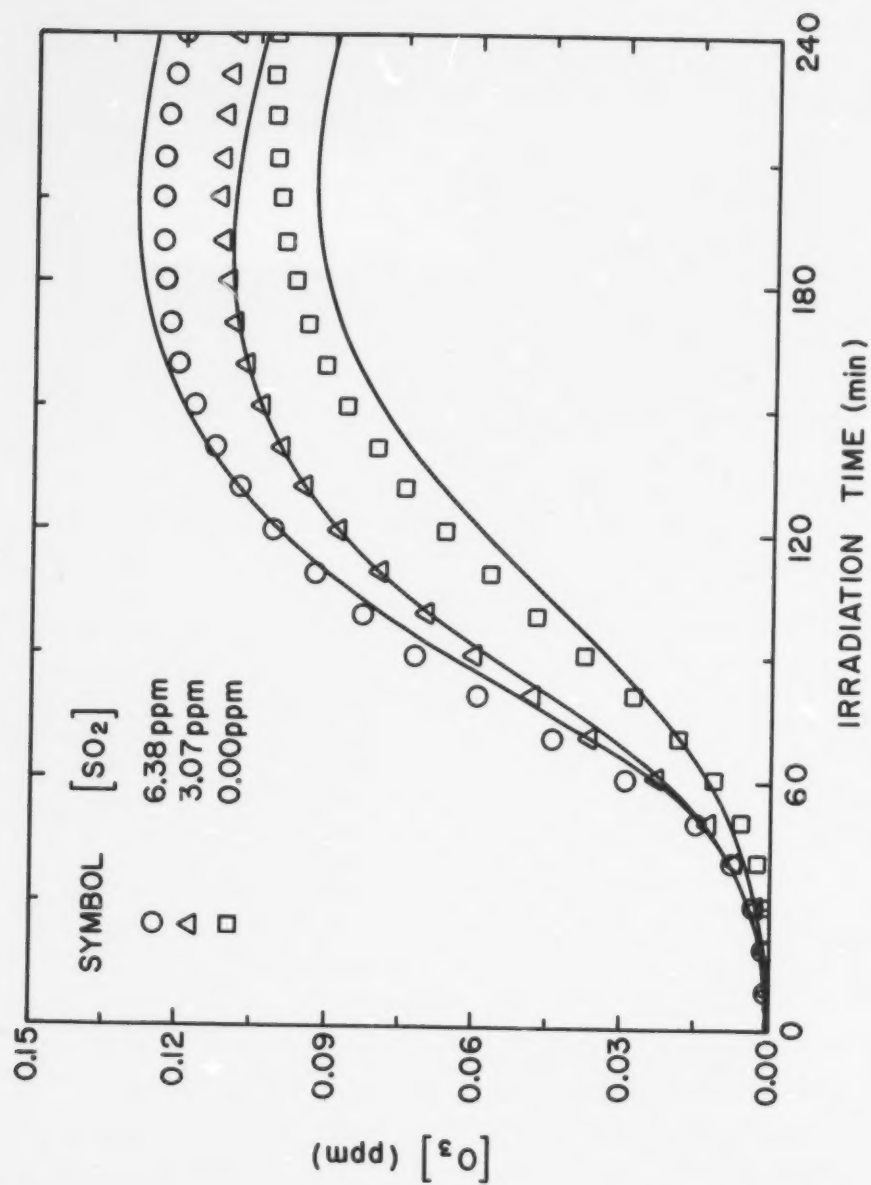


Figure 11. Comparison between modified model prediction and observed O_3 for experiments CH83216 (Δ), CH83222 ($\square$), and CH83244 ($\circ$).

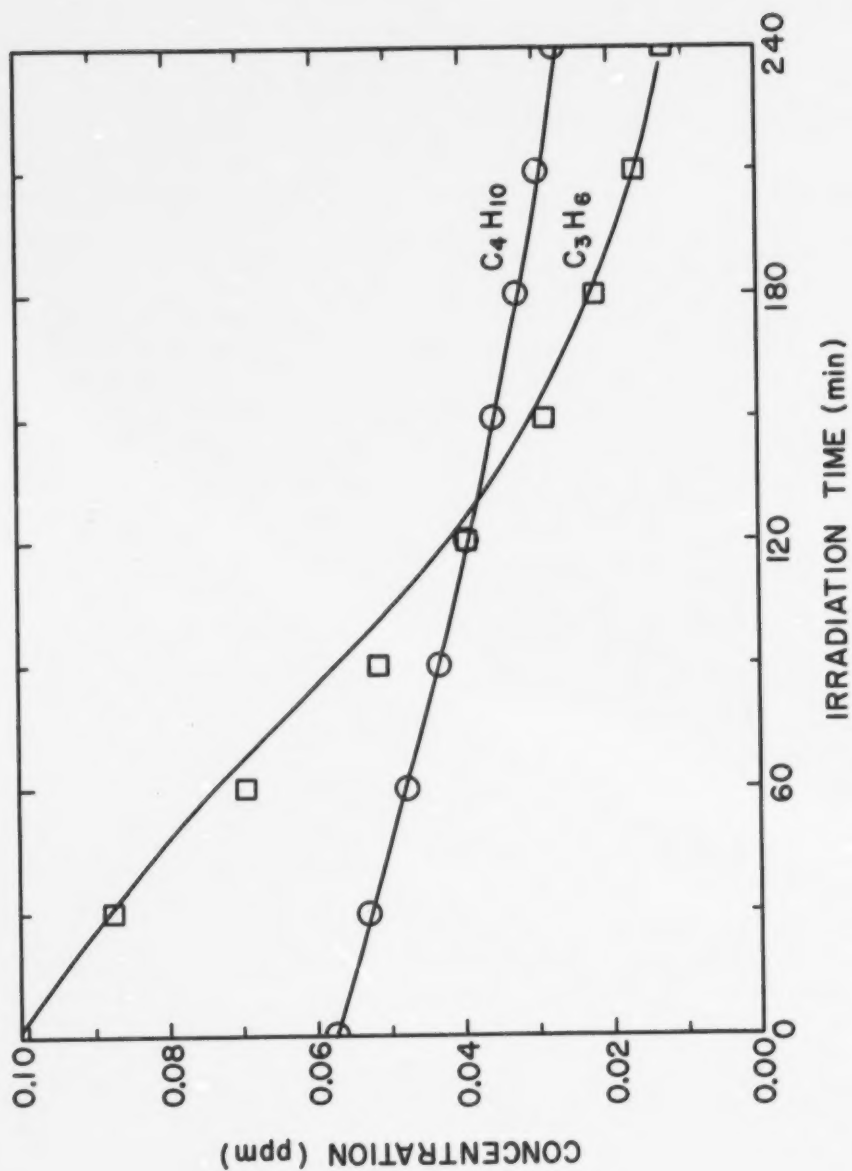


Figure 12. Modified model predictions and observed C_3H_6 ($\square$) and C_4H_{10} ($\circ$) for experiment with initial SO_2 concentration 6.38 ppm (experiment CH83244).

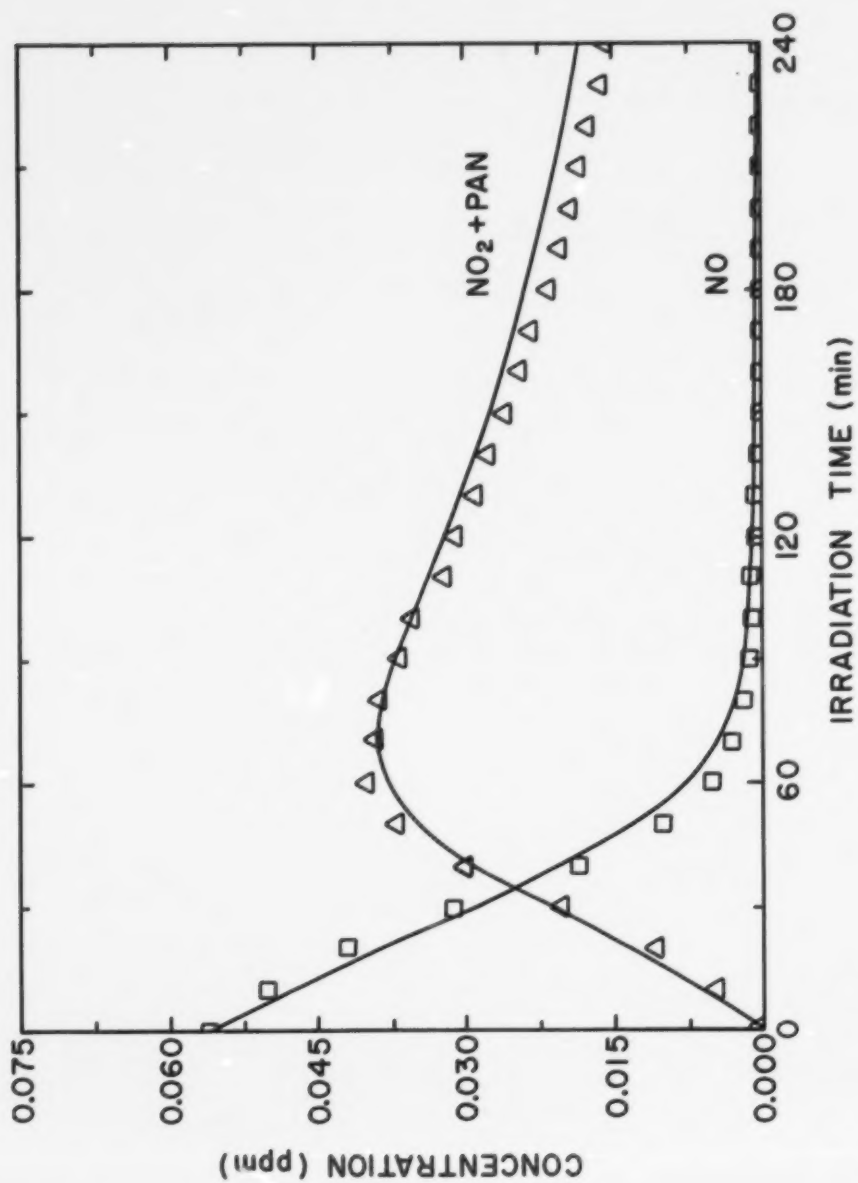


Figure 13. Modified model predictions and observed NO ($\square$) and NO₂ + PAN (Δ) for experiment CH83244.

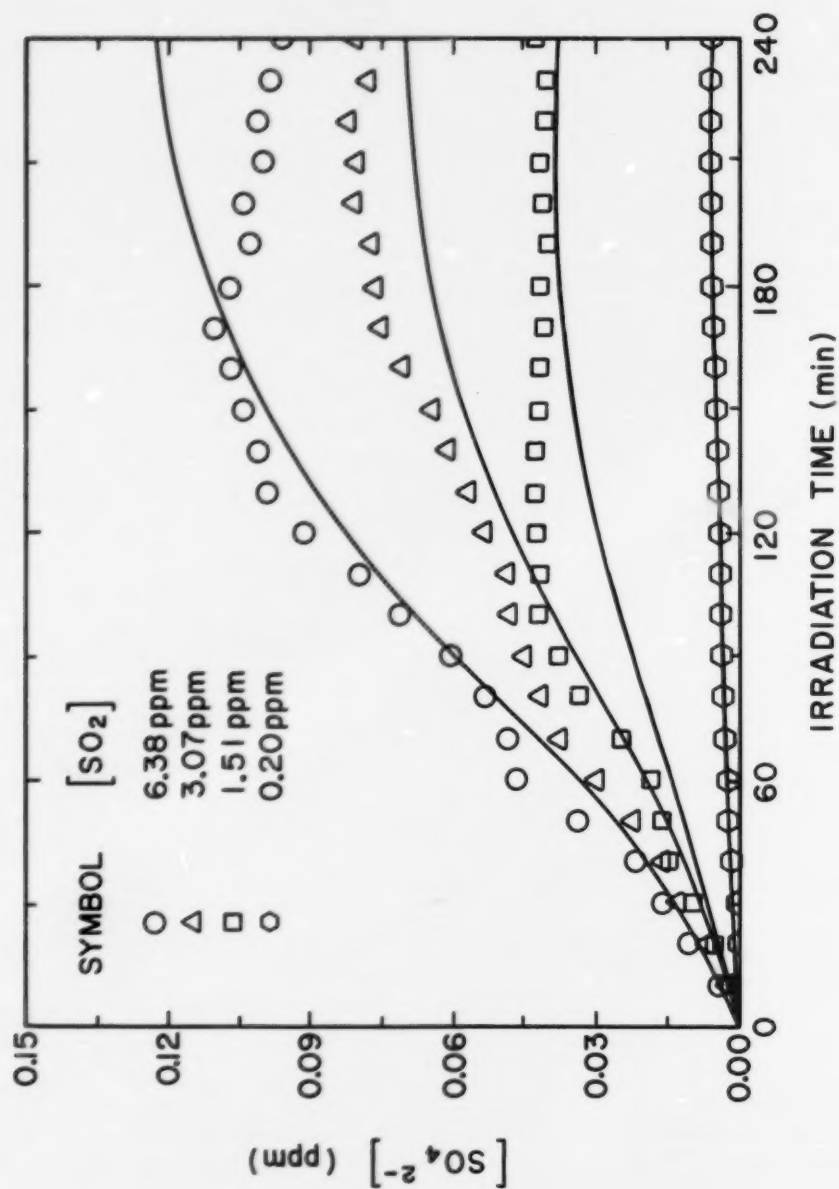


Figure 14. Comparison between model predictions and observed SO_4^{2-} concentration for experiments CH83165 (O), CH83161 (□), CH83216 (Δ), and CH83244 (O).

unique opportunity to examine the relationship between SO_2 concentration and the rate of SO_4^{2-} formation. This relationship is presented in Figure 15 for both the "wet" and "dry" experiments. The straight line represents perfect hydroxyl propagation, i.e., regeneration of one HO for each H_2SO_4 formed. As can be seen from Figure 15, the data deviate significantly from linear at the higher SO_2 concentrations. However, at low SO_2 concentration, when the consumption of HO by SO_2 is small ($<10\%$), the approximation of linearity between SO_2 concentration and SO_4^{2-} formation is valid.

It should be noted that the formation of HO_2 radicals in reaction (6) provides propagation of the HO chain only in the presence of excess NO. In the latter stages of these chamber experiments, there is insufficient NO to efficiently convert HO_2 to HO. Under these conditions, reaction of SO_2 with HO results in partial termination of the HO radical chain even though HO_2 is produced. Thus, a significant deviation from linearity was observed for the experiments with high SO_2 concentration even though SO_2 oxidation proceeds almost exclusively (98.5%) via reaction (6).

Obviously, the proposed mechanism is not unique. One cannot rule out other chemical reactions such as abstraction of weakly bonded hydrogen (aldehydes, peroxides, HONO, etc.) by HSO_4 or addition of this species to alkenes. However, the mechanism selected is simple, chemically consistent, and accurately reproduces the observed data over a wide range of SO_2 concentrations.

The rate data presented in Table 6 indicate that 98.5 percent of the time the HO- SO_2 reaction leads to HO_2 formation. This is consistent with the suggestion of Stockwell and Calvert (1983) that SO_2 termination of the HO radical may not be important in the free atmosphere. However, it must be emphasized that, although the observed HO termination (1.5%) is a small fraction of the total HO- SO_2 addition reaction, it significantly affects the temporal behavior and maximum levels of secondary pollutants.

Alkene + O_3 + SO_2

The addition of HO radicals to SO_2 can explain the bulk of the field measurements of SO_2 oxidation rate in the absence of clouds and precipitation. This mechanism, however, cannot explain nighttime SO_2 oxidation (Husar et al., 1978), the very high rates observed near urban areas (Alkezweeny and Powell, 1977), or the formation of organosulfur compounds (Eatough et al., 1981).

There are, however, additional gas phase pathways that have been suggested to contribute to SO_2 transformation in the atmosphere. One such pathway that may play a significant role in atmospheric SO_2 chemistry is oxidation in the presence of ozone and olefinic hydrocarbons. The rapid oxidation of SO_2 in SO_2 - O_3 -olefin-air mixtures was first demonstrated by Cox and Penkett (1971, 1972). These authors deduced

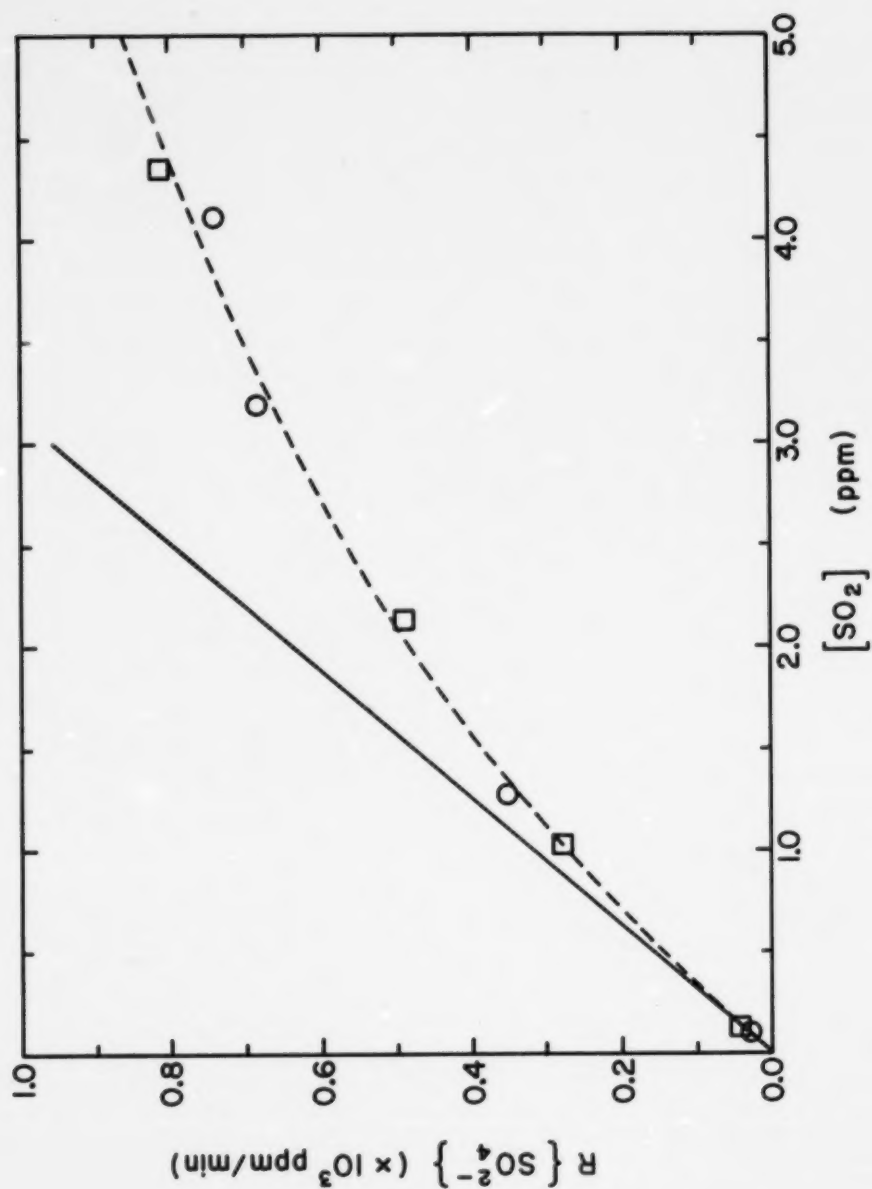


Figure 15. The average rate of SO_4^{2-} formation, $R\{\text{SO}_4^{2-}\}$, vs. average SO_2 concentration for "wet" (O) and "dry" ($\square$) experiments. The solid line represents perfect HO propagation.

that the SO_2 oxidation occurred via reaction with a product from the ozone-olefin reaction. These authors also observed that the SO_2 oxidation was inhibited in the presence of water vapor. Niki et al. (1977), Herron and Huie (1978), and Su et al. (1980) investigated various O_3 -olefin systems to determine the reaction pathway by examining the products produced in these systems in the absence and presence of SO_2 . The conclusion of these authors was that a significant fraction of the Criegee intermediate produced in O_3 -olefin reactions was sufficiently stabilized to thermalized biradicals that can react with SO_2 . Su et al. (1980) also presented spectroscopic evidence of an organosulfur compound in the aerosol produced.

Additional evidence for atmospheric SO_2 oxidation via the Criegee mechanism comes from chamber experiments conducted at the Tennessee Valley Authority (TVA) (Olszyna et al., 1983). The results from chamber runs in which dilute flue gas, from an operating coal-fired power plant, was irradiated in simulated atmospheres containing various levels of isobutene is shown in Figure 16. The excellent correlation between the SO_4^{2-} formation rate coefficient and the ozone-isobutene concentration product suggests SO_2 oxidation via a product of the ozone-isobutene reaction. The results from chamber experiments with propene as the reactive olefin also showed the same excellent correlation.

To evaluate the contribution of the hydroxyl addition mechanism to the observed SO_2 oxidation in these chamber runs, analytical procedures were developed to simultaneously measure both the SO_4^{2-} production and hydroxyl radical concentrations as a function of irradiation time (Olszyna and Meagher, 1983). The measured SO_4^{2-} formation rate coefficient and the SO_4^{2-} formation rate coefficient calculated from the measured hydroxyl radical concentration are shown in Figure 17 for experiments conducted at initial propene levels of 0.11 and 3.4 ppm respectively. For the high propene concentration experiment, the contribution of the HO addition mechanism to SO_2 oxidation is less than 5 percent of the observed. These results are experimental evidence for SO_2 oxidation by a non-hydroxyl mechanism. The excellent correlation between the SO_4^{2-} formation rate coefficient, corrected for the contribution from the hydroxyl addition mechanism, and the ozone-propene concentration product confirms SO_2 oxidation via a product of the ozone-propene reaction. To evaluate the effect of H_2O in these chamber simulations, the experiment at high propene concentration was repeated under simulated "dry" atmospheric conditions. The results of this experiment showed not only increased H_2SO_4 production but also evidence for the production of non-sulfate, sulfur aerosol (Olszyna and Meagher, 1983).

Atkinson and Lloyd (1984) reviewed the scientific literature on ozone-alkene systems and supported the following Criegee mechanism that was originally proposed by Calvert et al. (1978) to explain the observed SO_2 oxidation in O_3 -alkene- H_2O systems.

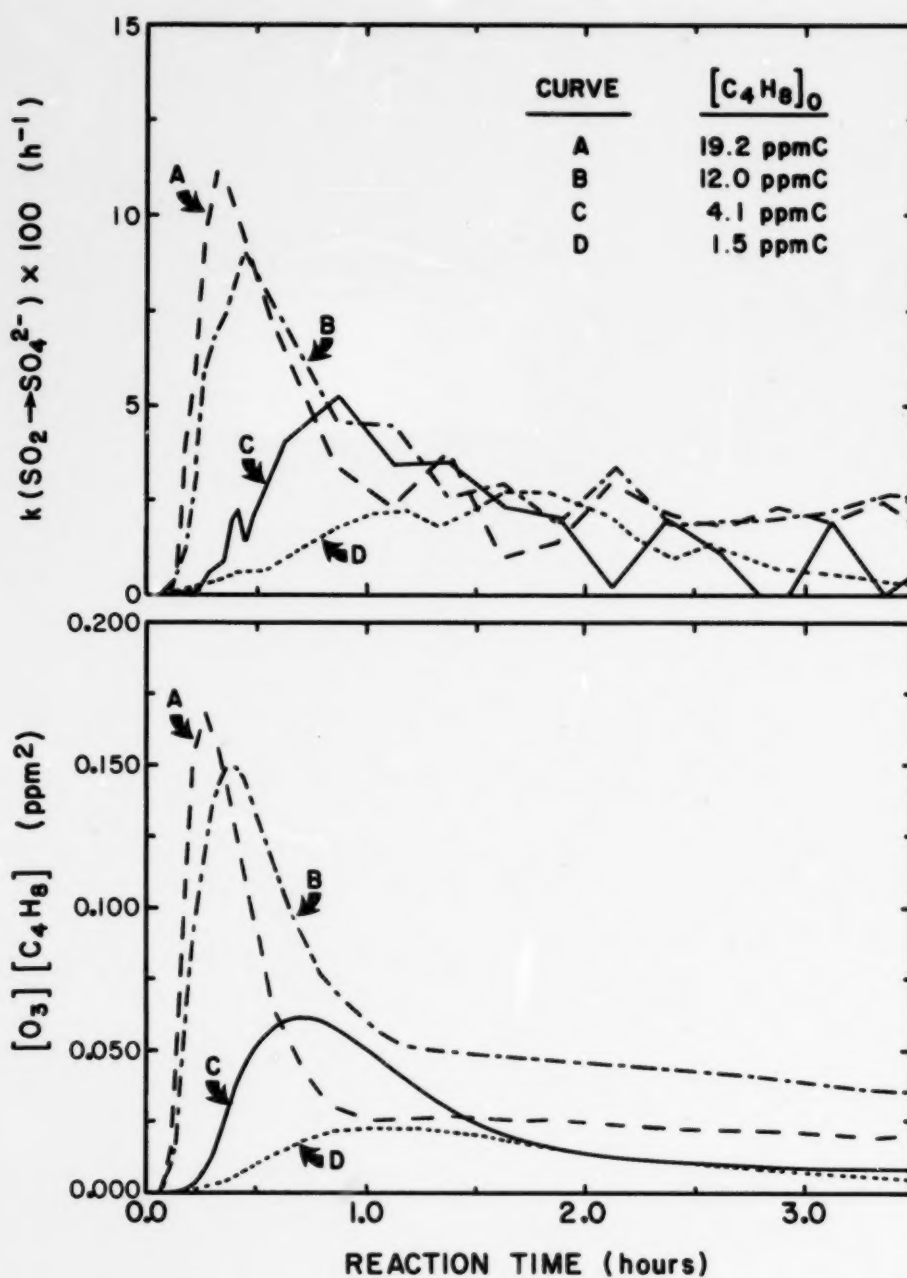


Figure 16. Reaction time profiles of pseudo first order rate constant for SO_2 conversion to SO_4^{2-} , $k(\text{SO}_2 \rightarrow \text{SO}_4^{2-})$, (upper curves) and O_3 -olefin product function, $[\text{O}_3][\text{C}_4\text{H}_8]$, (lower curves) for experiments with added isobutene (expressed in units of ppm Carbon).

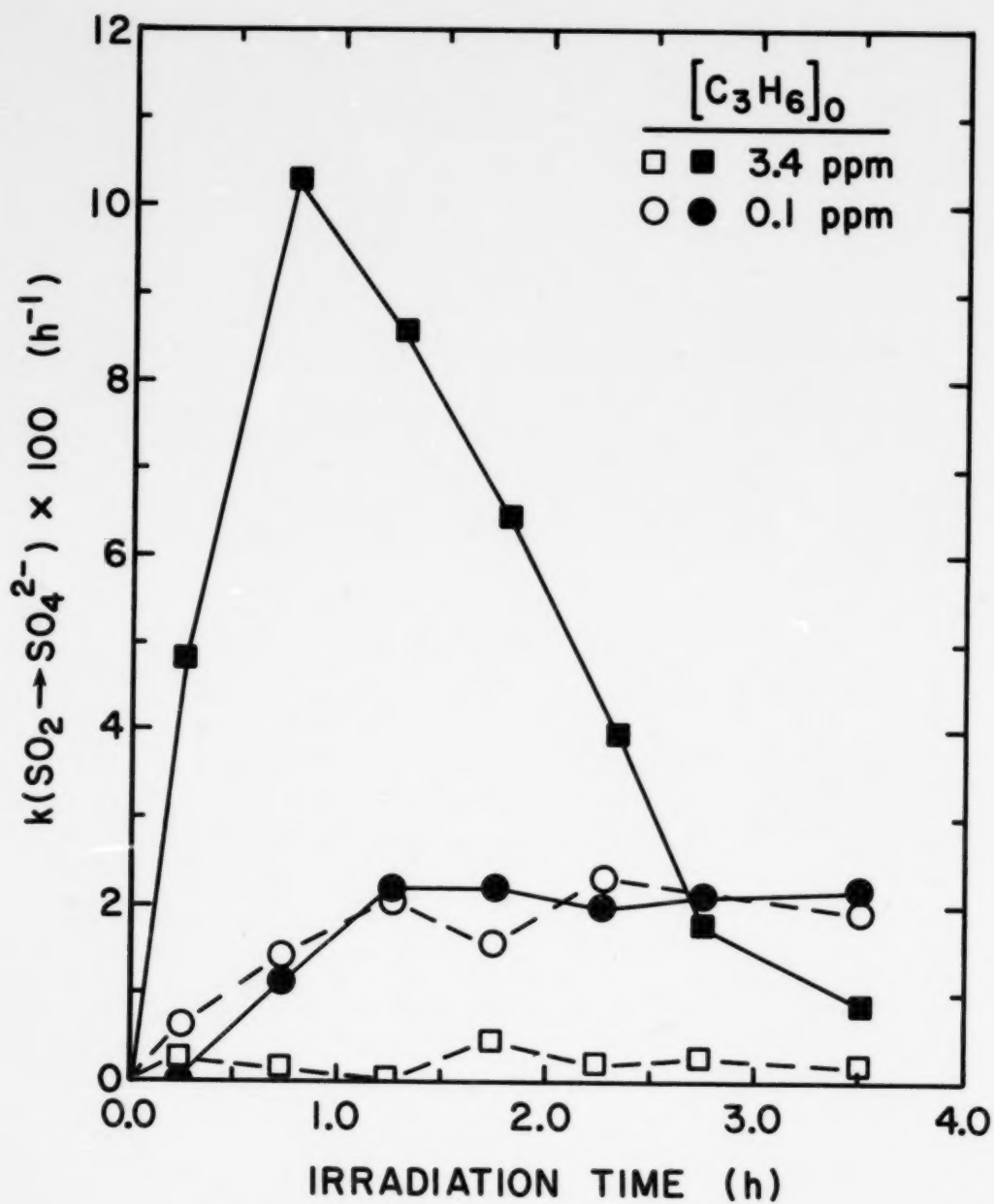
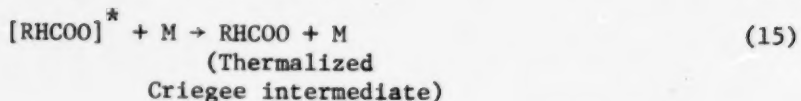
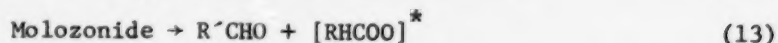
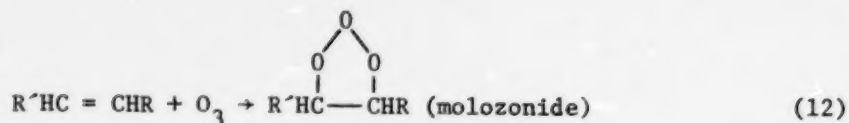
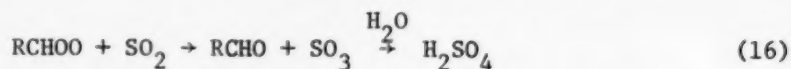


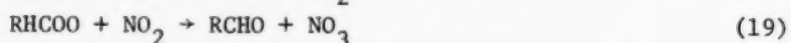
Figure 17. Plot of pseudo first order rate coefficient for SO_2 oxidation to SO_4^{2-} vs. irradiation time. The solid points are the time dependent rate coefficients measured from aerosol volume data correlated to SO_4^{2-} mass concentration. The open points are the calculated rate coefficients using the measured HO radical concentrations.



where $[RHCOO]^*$ denotes an energy-rich biradical that can be collisionally stabilized to the thermalized biradical, $RHCOO$. The thermalized Criegee intermediate can then react with either SO_2 to produce SO_3 , which is hydrolyzed to H_2SO_4 , or with H_2O to undergo rearrangement to a carboxylic acid.

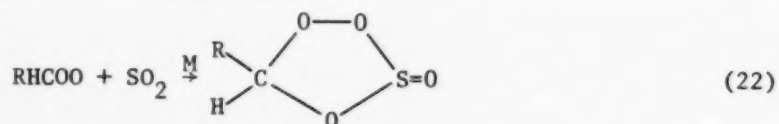


The Criegee intermediate can also react with other atmospheric constituents as follows:

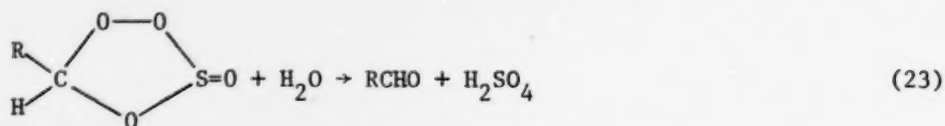


Atkinson and Lloyd (1984) combined the observations of Cox and Penkett (1972), Akimoto et al. (1979), and Su et al. (1980) and roughly estimated that the important atmospheric pathways for the Criegee intermediate were its reactions with NO_x , H_2O , and SO_2 .

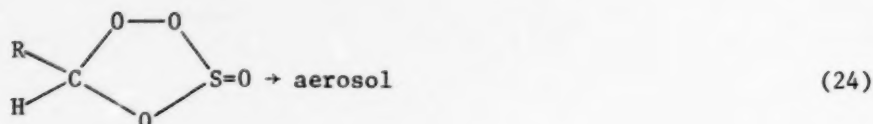
To explain the spectroscopic evidence of an organosulfur species (Su et al., 1980), as well as their own observations of metastable sulfur species (Martinez and Herron, 1980) in similar O_3 -alkene- SO_2 systems, Martinez and Herron (1981) proposed an addition reaction between SO_2 and Criegee intermediate to produce an organosulfur intermediate that was collisionally stabilized to an heterocyclic organosulfur species.



This heterocyclic species can then react with H_2O to produce H_2SO_4 .



Because the identity of the organosulfur species is not known, we shall assume that it can exist in both gas and particulate forms to explain the non-sulfate, sulfur aerosol produced in chamber experiments. To simplify the kinetic treatment of aerosol production in these systems, we propose the following reaction to empirically represent the formation of aerosol from the gas phase organosulfur species.



A steady state treatment of the intermediates in the above Criegee mechanism, using the SO_2 -Criegee reaction sequence proposed by Martinez and Herron, yields the following rate law for SO_2 oxidation.

$$-d[\text{SO}_2]/dt = k_{12}[\text{O}_3][\text{HC}] \cdot \text{A} \cdot \text{B} \quad (\text{XIII})$$

where

$k_{12} \equiv$ rate coefficient for the ozone-alkene reaction,

$\text{A} = k_{15}[\text{M}]/(k_{14} + k_{15}[\text{M}])$; fractional yield of the thermalized Criegee intermediate,

$\text{B} = k_{22}[\text{SO}_2]/(k_{22}[\text{SO}_2] + k_{17}[\text{H}_2\text{O}] + k_{18}[\text{NO}] + k_{19}[\text{NO}_2])$;
fraction of Criegee intermediates that react with SO_2 .

Applying the same steady treatment as above yields the following rate law for H_2SO_4 formation.

$$d[\text{H}_2\text{SO}_4]/dt = k_{12}[\text{O}_3][\text{HC}] \cdot \text{A} \cdot \text{B} \cdot \text{C} \quad (\text{XIV})$$

where k_{12} , A, and B are the same as above

and

$$C = k_{23}[H_2O]/(k_{23}[H_2O] + k_{24}); \text{ fraction of the } SO_2\text{-Criegee adduct intermediates that are hydrolyzed to } H_2SO_4.$$

Conversely, the production of organosulfur aerosols can be described by the following rate law

$$d[\text{organosulfur aerosol}]/dt = k_{12}[O_3][HC] \cdot A \cdot B \cdot D \quad (XV)$$

where k_{12} , A, and B are the same as above

and

$$D = k_{24}/(k_{23}[H_2O] + k_{24}); \text{ fraction of the } SO_2\text{-Criegee adduct intermediates that produce organosulfur aerosol.}$$

Equation XIV states that the rate of production of H_2SO_4 from SO_2 oxidation via the Criegee mechanism is a function of six different terms. Because there are little experimental data on these systems from which the terms A, B, and C can be determined, the importance of this non-hydroxyl pathway for H_2SO_4 production in the atmosphere is difficult to evaluate.

The results of chamber experiments conducted under a simulated atmospheric humidity level of 40 percent indicated that all of the SO_2 -Criegee adduct intermediates in the propene-hydrocarbon system were hydrolyzed to H_2SO_4 (Olszyna and Meagher, 1983). The results of a chamber run conducted under a simulated "dry" atmosphere are in qualitative agreement with that predicted by equations XIV and XV. The competition between SO_2 and H_2O for the Criegee intermediate (term B in equation XIV) predicts an increase in H_2SO_4 production as was observed. The competition between H_2O and particulate formation for the SO_2 -Criegee adduct species (term D in equation XV) predicts an increase in organosulfur aerosol formation. To determine that the observed aerosol production increase was due to the production of organosulfur aerosols, this "dry" chamber experiment has recently been repeated with measurements for total aerosol volume and analysis of the aerosol produced for both total S content by Proton Induced X-ray Emission (PIXE) and SO_4^{2-} content by Ion Chromatography (IC). The results are shown in Figure 18. These results support our previous suggestion (Olszyna and Meagher, 1983) that both sulfate and non-sulfate sulfur aerosols are produced in this system.

Although the identity of this non-sulfate aerosol is still not known, the experimental evidence indicates that both sulfate and nonsulfate aerosols can be produced from atmospheric SO_2 reaction via the Criegee mechanism. Eatough (1982) has observed that nonsulfate aerosols formed in the O_3 -alkene- SO_2 system convert spontaneously at room temperature to sulfate. The oxidation process occurs at room temperature over a period of days or weeks. Ambient air and chamber filter samples are routinely stored for weeks prior to analysis; thus, S(IV) aerosols present in the ambient or produced in laboratory experiments may be analyzed and reported as sulfate.

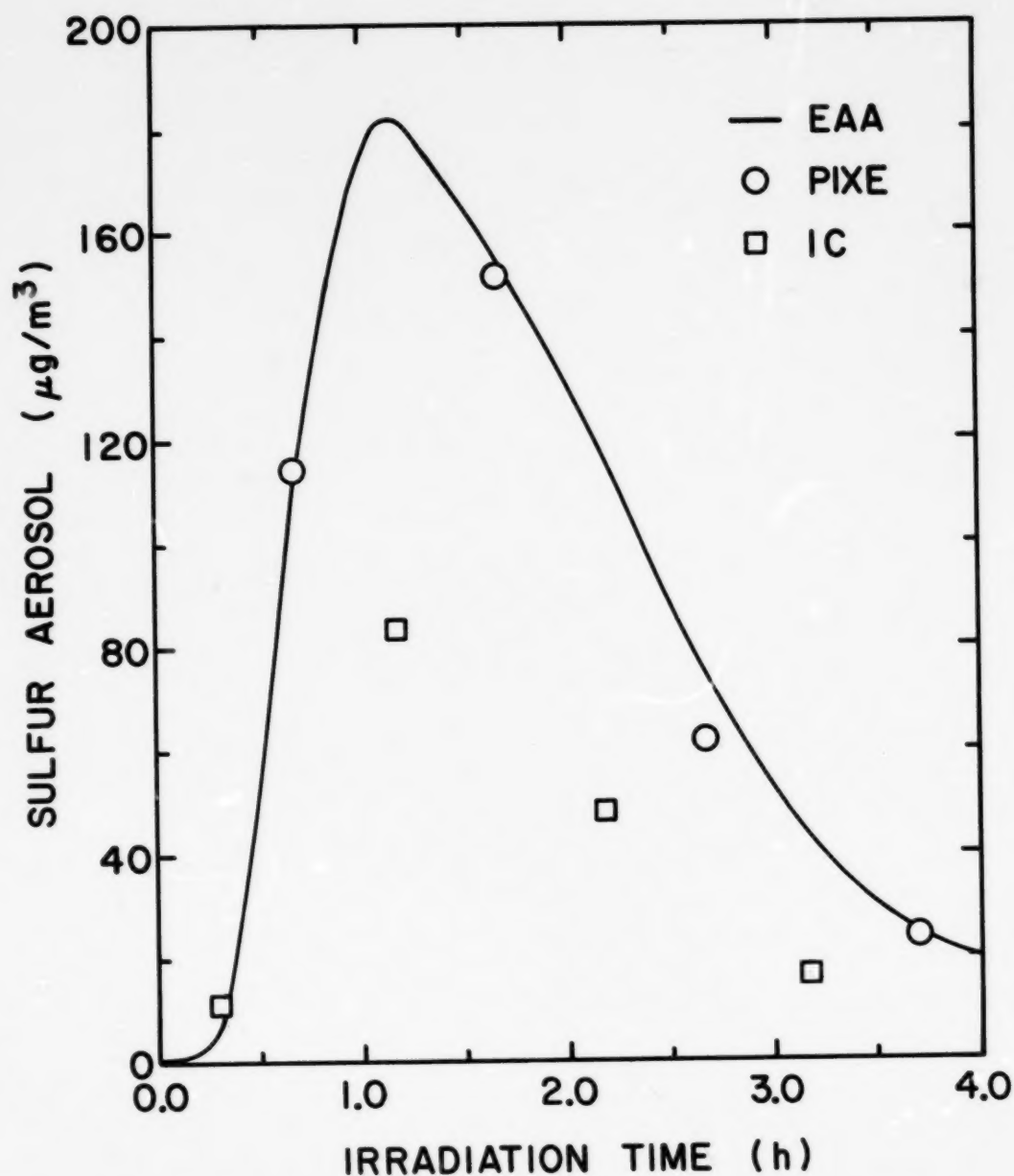


Figure 18. Time profiles of sulfur-aerosol production in chamber simulation in "dry" atmosphere with initial SO_2 , NO , and propene levels of 0.2, 0.05, and 3.1 ppm respectively. The squares are SO_4^{2-} concentrations in aerosol samples analyzed by Ion Chromatography (IC). The circles are S concentrations, reported as SO_4^{2-} , in aerosol samples analyzed by Proton Induced X-ray Emission (PIXE). The solid curve is aerosol concentration, reported as SO_4^{2-} , calculated from aerosol volume monitored by an Electric Aerosol Analyzer (EAA).

From the above discussion, it is obvious that the O_3 -alkene- SO_2 chemical system is poorly understood. The validity of the various mechanisms proposed must be further tested before one can be selected with confidence.

Model Simulations

Atkinson et al. (1982) were able to fit the smog chamber data of Miller (1978) using a simple sulfur chemistry scheme composed of reactions 1 and 16. As stated above, the insensitivity of the data set to the products of the $HO + SO_2$ reaction allowed for good agreement although the reaction was assumed to result in HO termination. The model also performed satisfactorily at the higher hydrocarbon concentrations where the Criegee mechanism (reaction 16) would be expected to play a role.

To further test and evaluate this simple scheme for SO_2 oxidation by the Criegee route, model calculations were performed and compared with data obtained in TVA chamber experiments. As was previously the case, these experiments were conducted using NO_x -propylene-butane- SO_2 -air mixtures. The experimental conditions for the two experiments selected are given in Table 7. The model used was the one described in Appendix B which included the revised $HO + SO_2$ mechanism discussed above. A small supplementary HO source was used in these calculations for reasons discussed above. An HO production rate of 1.5×10^{-6} ppm min^{-1} was used for CH82196 while a value of 2.5×10^{-6} ppm min^{-1} was used for CH82292.

A comparison of model estimates and chamber data is presented in Figures 19-22. The agreement is excellent for all species measured. The model predicts that the bulk of the measured SO_4^{2-} is formed via the Criegee mechanism with 78 and 64 percent of the SO_4^{2-} present at the end of the simulation formed by this mechanism in experiments CH82196 and CH82292 respectively. Thus, this mechanism appears to perform well over a wide range of precursor concentrations.

This mechanism does not, however, explain the formation of non-sulfate sulfur aerosols. The development of a mechanism to explain these species must await additional data.

KINETIC MECHANISM - SO_2 OXIDATION

A summary of the mechanism and a listing of the rate parameter requirements for the modeling of SO_2 oxidation are presented in Table 8. The suggested mechanism utilized the $HO + SO_2$ reaction scheme described in this report and the Criegee mechanism and rate data of Atkinson et al. (1982). The reactions and rate data given must be combined with a free radical photochemical scheme describing atmospheric NO_x /hydrocarbon reactions. Several such schemes are available (see for example, Falls et al., 1979; Atkinson et al., 1982; and Killus and Whitten, 1983) and can easily be modified to accommodate this mechanism.

TABLE 7. SUMMARY OF INITIAL CONDITIONS AND EXPERIMENTAL PARAMETERS

Experiment number	Initial concentrations (ppm)						k_d^a (min^{-1})	$J\{\text{NO}_2\}^b$ (min^{-1})	Temp. (°C)	
	SO ₂	NO	NO ₂	C ₃ H ₆	C ₄ H ₁₀	H ₂ O				
CH82292	0.155	0.0518	0.0015	0.511	0.0613	0.25	11,500	2.68×10^{-3}	0.201	29
CH82196	0.159	0.0471	0.0005	0.755	0.0604	0.25	12,400	2.73×10^{-3}	0.183	37

^aDilution rate coefficient.^bNO₂ photolytic rate coefficient.

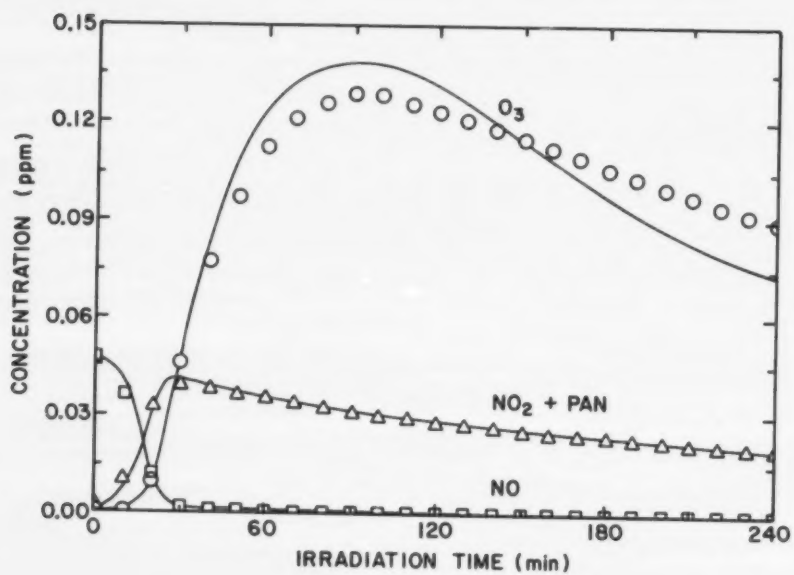
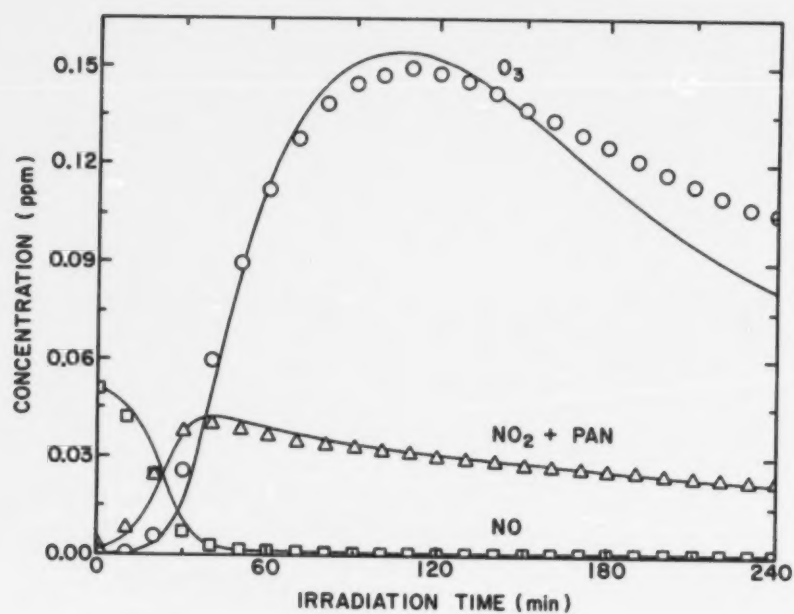


Figure 19. Comparison of experimental results and model predictions (solid lines) for experiments CH82292 (upper) and CH82196 (lower).

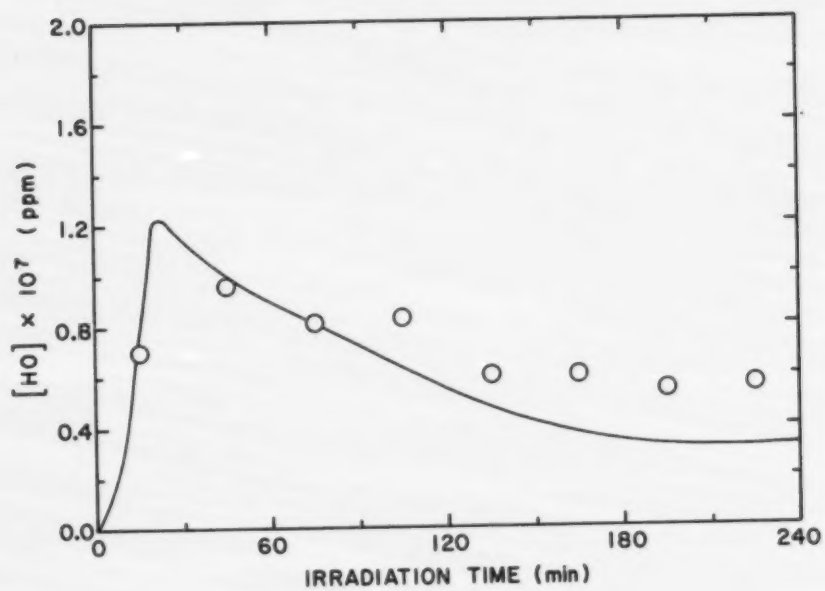
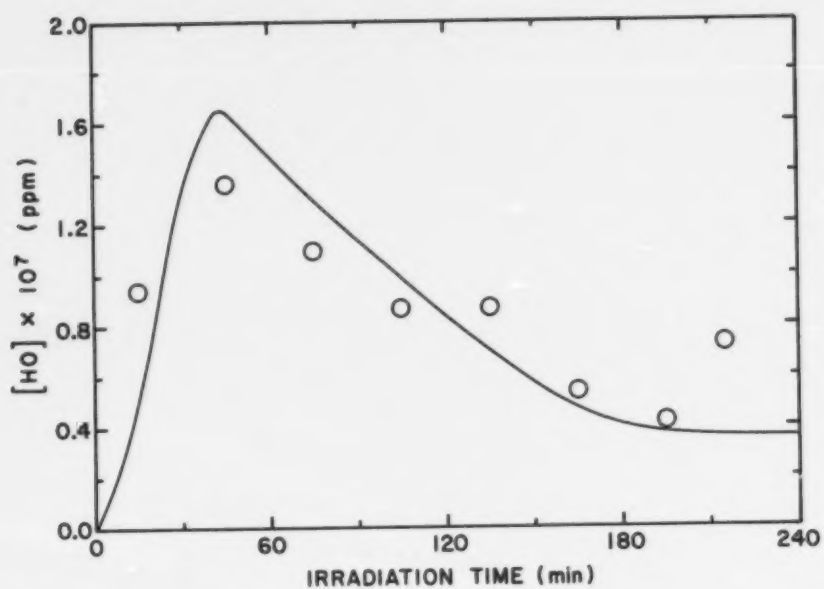


Figure 20. Comparison of experimental results and model predictions (solid lines) for experiments CH82292 (upper) and CH82196 (lower).

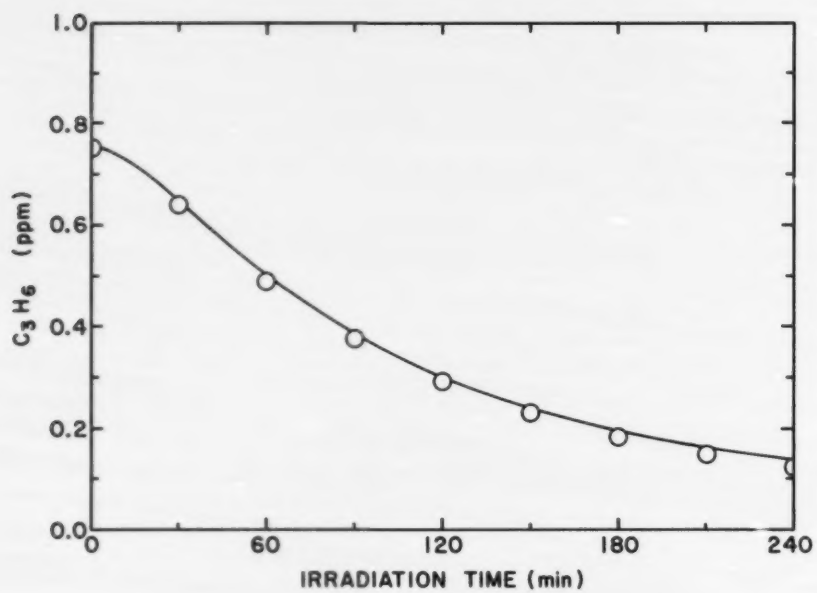
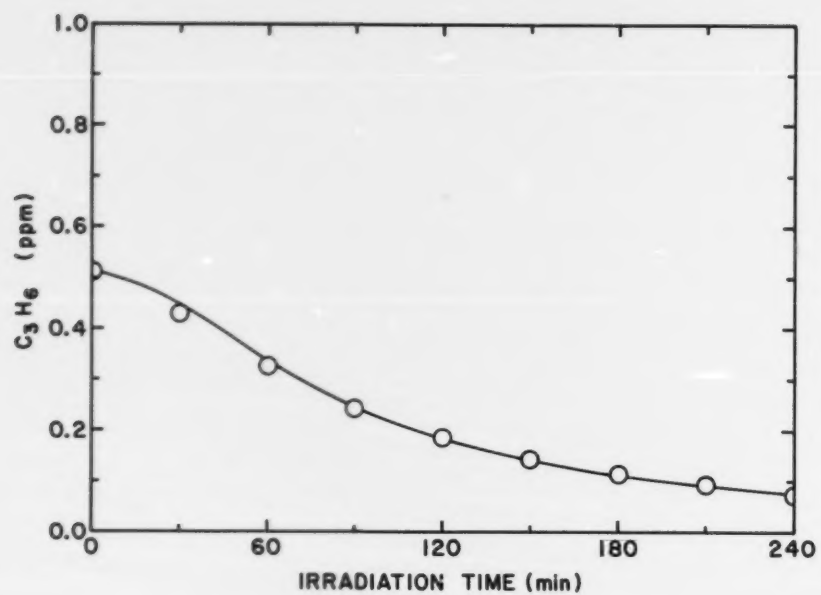


Figure 21. Comparison of experimental results and model predictions (solid lines) for experiments CH82292 (upper) and CH82196 (lower).

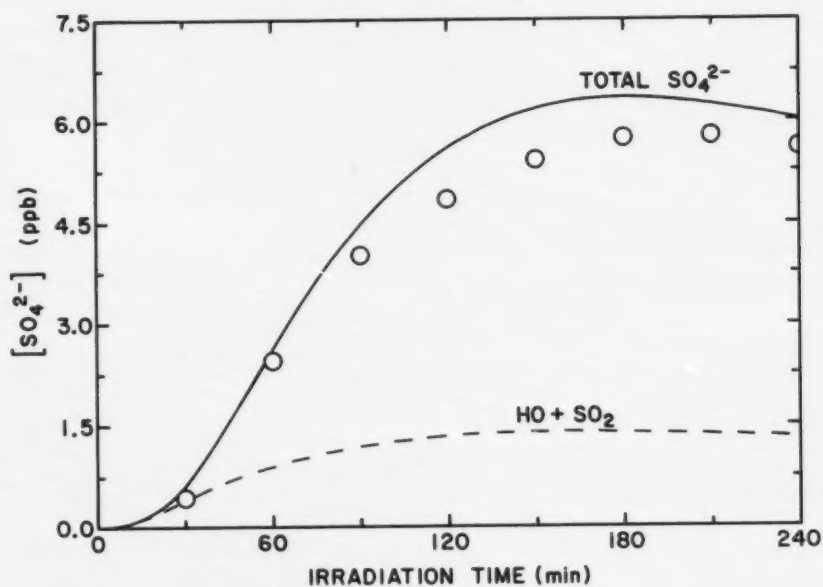
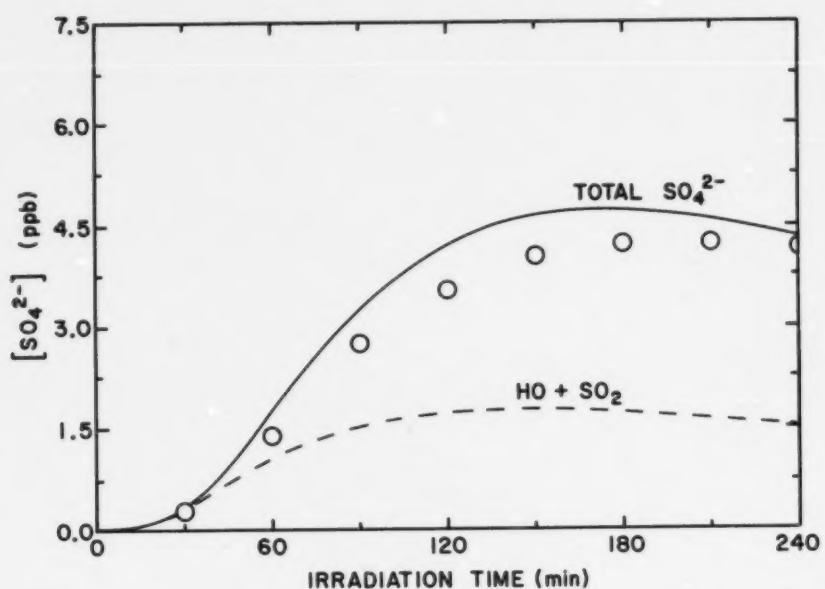


Figure 22. Comparison of experimental results and model predictions (solid lines) for experiments CH82292 (upper) and CH82196 (lower). Dashed line indicates model predictions of contribution to SO_4^{2-} concentration from hydroxyl mechanism.

TABLE 8. CHEMICAL MECHANISM AND RATE DATA FOR SO₂ OXIDATION IN THE ATMOSPHERE

Reaction		k (ppm ⁻¹ min ⁻¹)	Reference
HO + SO ₂	O ₂ , H ₂ O →	1.18 x 10 ¹³ T ⁻⁴	Atkinson and Lloyd, 1984*
HO + SO ₂	O ₂ →	1.8 x 10 ¹¹ T ⁻⁴	" "
HSO ₅ + NO	→	3.05 x 10 ⁶ T ⁻¹	This work
HSO ₄ + HO ₂	→	7.63 x 10 ⁴ T ⁻¹	"
HSO ₄ + O ₃	→	3.05 x 10 ³ T ⁻¹	"
RCHO + SO ₂	H ₂ O →	3.0 x 10 ⁴ T ⁻¹	Atkinson et al., 1982

*The formula provided by these authors was used to calculate the total HO + SO₂ rate constant. The k₆/k₇ ratio obtained in this work was applied to their value. This ratio is assumed to be independent of temperature.

The kinetic schemes might need to be modified to accomodate computational limitations in larger models incorporating detailed transport. In such cases, the condensed mechanism must realistically simulate the HO, HO₂ chemistry if the proposed scheme for SO₂ chemistry is to be effective. Such models should be carefully tested to verify this ability.

This mechanism is suitable for both rural and urban simulations because it has been tested over a wide range of hydrocarbon/NO_x ratios. The hydroxyl radical mechanism will dominate at low hydrocarbon^x/NO_x ratios with the Criegee mechanism playing an increasing role with high hydrocarbon concentrations. The relative contribution of these two mechanisms to SO₄²⁻ formation is shown as a function of hydrocarbon concentration in Figure 23. It is of interest to note that, although the relative importance of the two mechanisms shifts dramatically in the region for 0.5-3 ppmC, the effect on SO₄²⁻ production is small.

The combination of these two SO₂ oxidation mechanisms provides the best available representation of this process. Additional data are obviously needed, especially at high hydrocarbon/NO_x ratios, to resolve the remaining uncertainties.

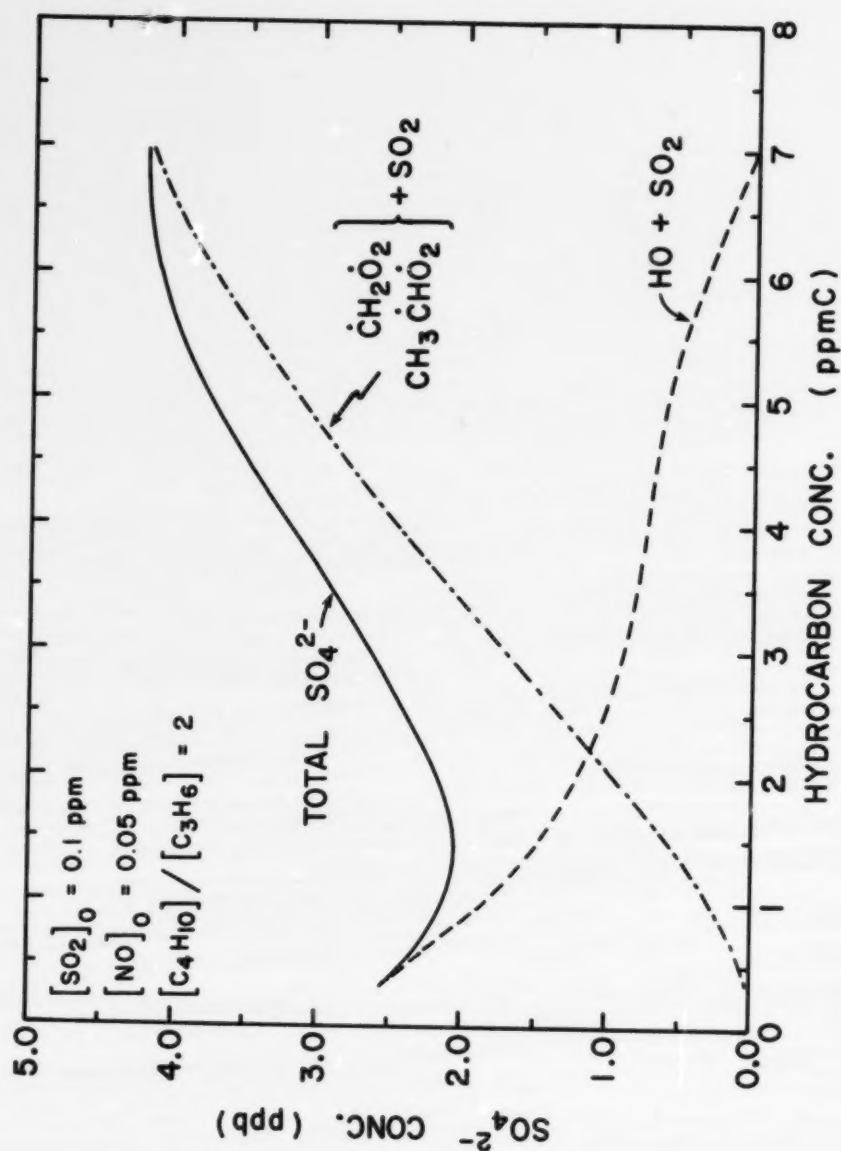


Figure 23. Relative contributions of hydroxyl and alkene-ozone mechanisms to SO_4^{2-} concentration after four hours as a function of initial hydrocarbon ($C_3H_6 + C_4H_{10}$) concentration.

CONCLUSIONS AND RECOMMENDATIONS

Two options have been provided for simulating SO_2 chemistry in atmospheric models. Both schemes are intended for gas phase oxidation and do not address cloud or precipitation chemistry. The option selected for a particular application depends on the averaging period, availability of input data, and computational restrictions.

The empirical model provides a simple alternative to more complex kinetic models, the use of which may be precluded by lack of input data or computational restrictions. The SO_2 rate coefficient predictions are based on an extensive set of field measurements, the diurnal and seasonal variations of which are faithfully reproduced. This model is intended to represent the average situation. It should not be expected to exhibit significant skill in reproducing individual events.

The kinetic model provides significantly more insight into the complex chemical interactions that control SO_2 oxidation in the atmosphere. When coupled with a comprehensive free radical photochemical model, the recommended scheme should successfully reproduce observed SO_4^{2-} formation over a wide range of NO_x and hydrocarbon concentrations. This kinetic scheme is more appropriate to assessments requiring estimates for fine temporal and spatial scales.

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APPENDIX A

CHAMBER DESCRIPTION

The 1100 ft³ photochemical reaction chamber (Figure A-1) is a 10-sided cylinder constructed from aluminum frame, mounted on a transportable chassis. The chamber walls are made of 0.13-mm FEP Teflon film, which transmits tropospheric solar radiation ($\lambda > 290$ nm) and also most of the infrared radiation, thus reducing "greenhouse" effects. All interior elements of the chamber are constructed from Teflon, Teflon-filled asbestos, and to a lesser extent stainless steel. Details on the construction of the photochemical reaction chamber have been reported previously (Stockburger and Meagher, 1979).

When experiments are not being conducted, the chamber is flushed continuously with purified ambient air at a rate of 180 l/min. The cleanup system consists of a Hankinson Model 505 dehumidifier, a series of traps and filters, a General Cable Corporation puregas heatless dryer Model HE200-120-054, and a stainless steel filter element that removes 99.999 percent of particles larger than 0.3 micron. The purification system reduces particle number density to about 200 particles/cm³, removes all measurable quantities of O₃ and NO (< 1 ppb and < 5 ppb respectively), and reduces the dewpoint to a level of at least 55°C below the ambient temperature. The air purification system does allow passage of some measurable quantities of nonmethane hydrocarbons (approximately 30 to 50 ppbC, which is typical of rural air in southeastern United States). To minimize any wall contamination effects, the chamber is irradiated (with flushing) between experiments. Chamber cleanliness is checked periodically by performing blank runs. Chamber characteristics are checked periodically by performing a "standard" experiment.

Solar radiation is simulated with a combination of GE 40-watt fluorescent black lamps (F40BL) and GE 40-watt sun lamps (FS40) used in a 3:1 ratio respectively. The actual light intensity is determined utilizing the NO₂-N₂ actinometry method as described by Jeffries et al. (1975).

SAMPLING PROCEDURES

To reduce or eliminate sample losses, the chamber is located over the instruments' enclosure and all sampling lines are Teflon and/or stainless steel. The sample probes are positioned in the chamber to minimize any bias due to wall effects (Figure A-2). To maximize homogeneous sampling all the measurement parameters are conducted at a given radius from the center of the chamber. Temperature is monitored at three vertically equidistant points from the top to the chamber floor. Gas and particulate samples are withdrawn at a height of 5 feet from the chamber floor through one-half-inch o.d. stainless steel tubing. All continuously monitored gaseous species (gaseous S, SO₂, CO, NO_x, O₃,

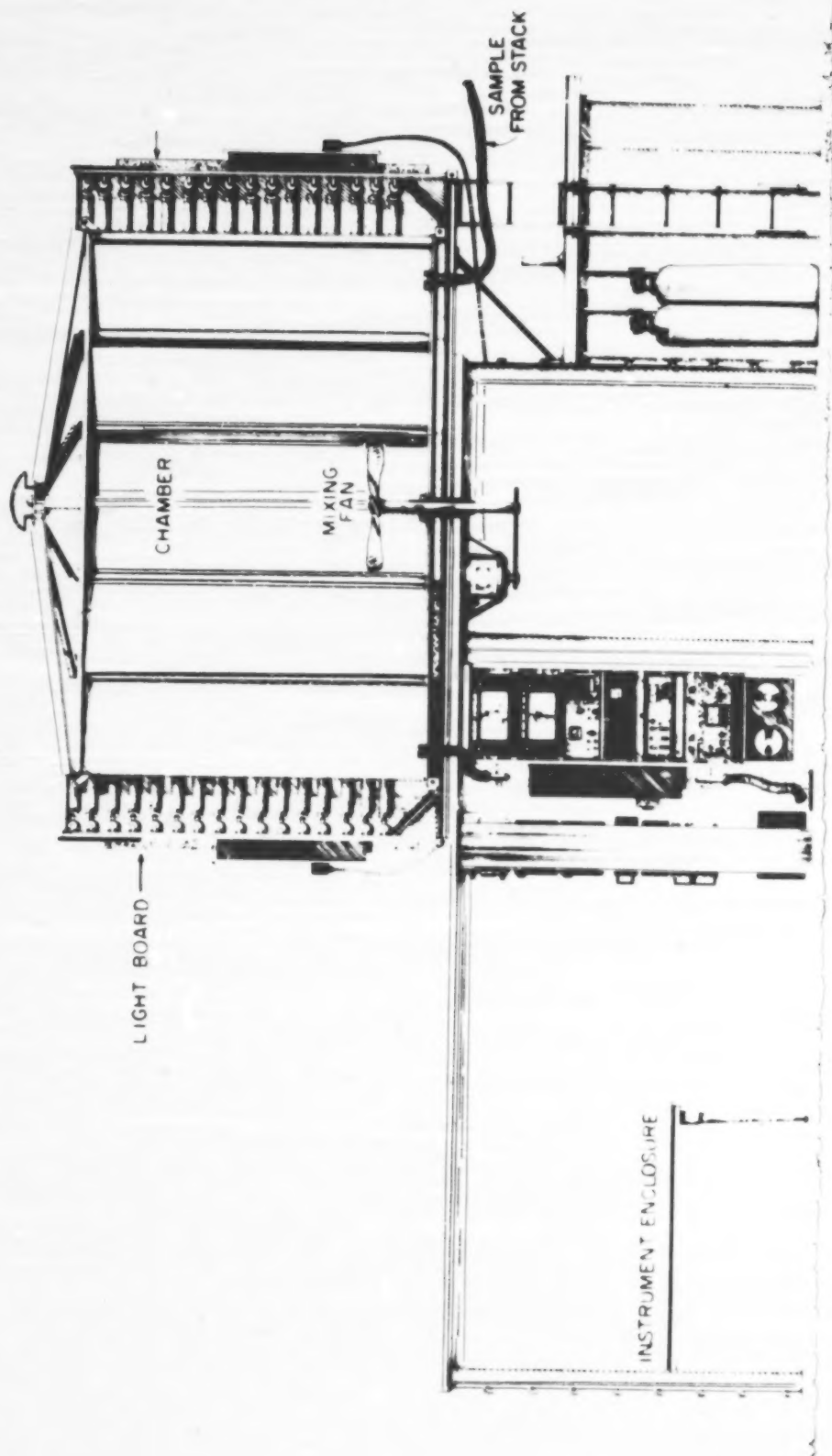


Figure A-1. Cross-sectional view of TVA smog chamber showing location of light boards and instrument enclosure.

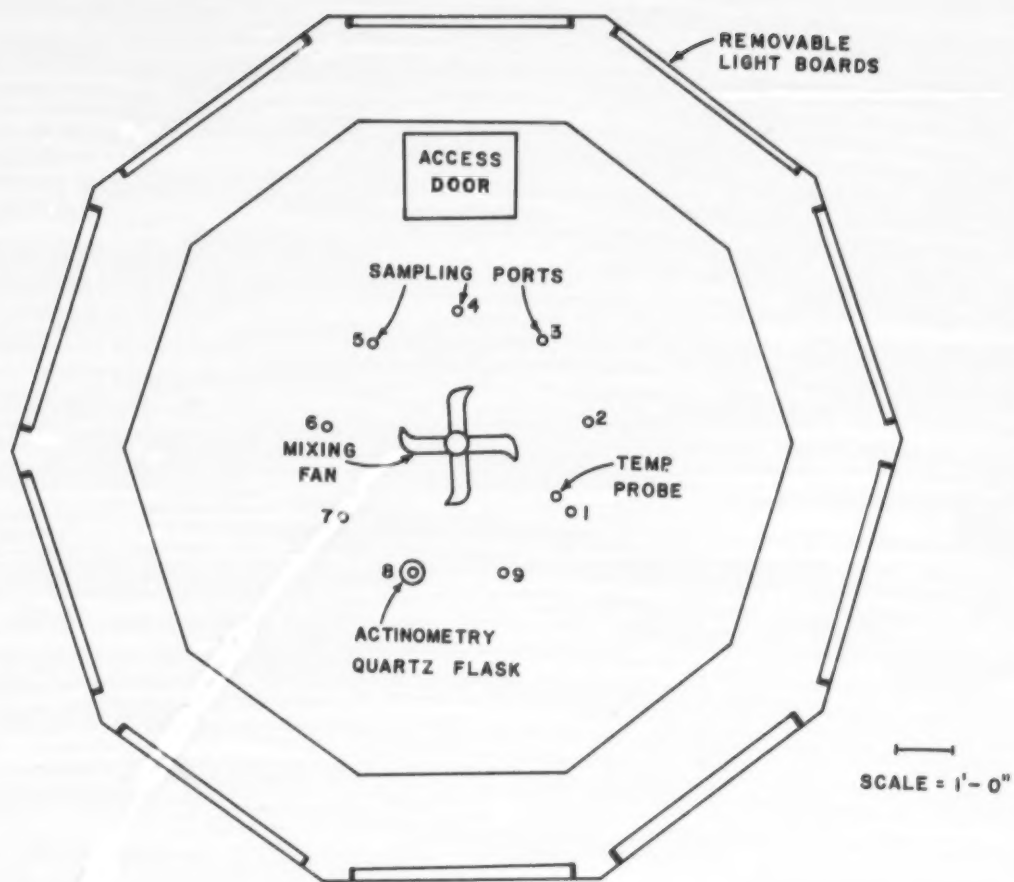


Figure A-2. Floorplan of TVA smog chamber of surrounding light boards.

and H_2O) pass through a common sampling probe. In this way, a high flow rate is achieved through a one-half-inch diameter line with minimum surface loss and transport time to the monitors. Transport time is estimated to be less than 5 seconds. Air samples are withdrawn periodically during irradiation from the chamber by passing it through a Teflon filter to remove aerosols and an MnO_2 catalytic scrubber to remove reactive products (e.g., ozone) and collected in specially treated stainless steel canisters. The hydrocarbon content of the air samples is analyzed using a Hewlett-Packard 5880 FID gas chromatograph. This procedure allows a characterization of the hydrocarbon content as well as the determination of the loss rates for specific hydrocarbon species. Because of the different modes of operation of the aerosol monitors, there are different probe positions for different aerosol instruments. Filter samples and nephelometer readings, which are taken only once an hour because of their excessive sampling volume, are sampled separately. A mass flow meter downstream monitors the volume of air sampled. The quartz flask, which serves as actinometer vessel to measure light intensity, is placed on the same radius as the other sampling probes and at half chamber height.

ANALYTICAL PROCEDURES

The following procedure was used to conduct the experiments. Any or all of the following reagent gases were added to the chamber in amounts to simulate a specific chosen air quality: NO_x , hydrocarbon, CO , O_3 , SO_2 , and H_2O . Flue gas from a coal-fired power plant stack was transferred through a heated sampling line into the chamber and mixed with chamber air by a mechanical stirrer. When the desired concentration was achieved, the stirrer was turned off and the system was allowed another 30 minutes equilibrium time to ensure homogeneous gas mixture. Purified air was added into the chamber to replenish the volume lost to sampling and/or to simulate different dilution rates. The chamber was operated at slight positive pressure to avoid contamination from ambient air.

Continuous measurements of NO_x , O_3 , SO_2 , CO , Aiken nuclei (CN), temperature (T), dewpoint (DP), submicron particle size distributions (EAA) and dilution air flow were conducted before turning the lights on (to insure no dark reaction occurred) until several hours after the lights were turned off (to obtain wall loss rate coefficients for SO_2 , O_3 , and SO_4^{2-}). Aerosol samples were collected on a Teflon filter (Fluoropore, 1 μm pore size, type FA) once an hour and analyzed for SO_4^{2-} by ion chromatography. Air samples for hydrocarbon analysis were withdrawn at 30-minute intervals during irradiation. The hydrocarbon content of the air samples was determined using a Hewlett-Packard 5880 gas chromatograph equipped with a flame ionization detector utilizing a 6 m long 1.6 mm O.D. column packed with n-octane on poracil C 100/120 mesh. Background measurements for hydrocarbon content and light scattering (b_{scat}) were also conducted. A detailed list of the instruments and their mode of operation is shown in Table A-1.

Table A-1. INSTRUMENTS USED FOR THE TVA SMOG CHAMBER STUDY

Parameter	Analytical Technique	Operational Mode	Manufacturer, Model
Gaseous sulfur	Flame photometry	Continuous	Meloy, 285
SO ₂	Pulsed fluorescence	Continuous	TECO, 43D
CO	Correlation spectrometry	Continuous	Dasibi, 3003
NO, NO _x	Chemiluminescence (O ₃ + NO)	Continuous	Monitor Lab, 8440
O ₃	Chemiluminescence (O ₃ + C ₂ H ₄) Spectrophotometric	Continuous	Monitor Lab, 8410 McMillan, 1100-3 Dasibi, 1003-AAS
Condensation (Aiken) nuclei	Light attenuation by water droplets condensed on CN's	Continuous	Environment One, Rich 200
Temperature	Thermistor	Continuous	Thermo Electric, Elph 111
Dewpoint	Hygrometer	Continuous	General Eastern Inst., 1100 DP
b _{scat}	Light attenuation (Integrated nephelometer)	Once an hour	MRI, 1550B
SO ₄ ⁼	Filter collection/Ion chromatograph	Once an hour	Dionex, 10

TABLE A-1 (continued)

Parameter	Analytical Technique	Operational Mode	Manufacturer, Model
Particle size distribution (0.02 - 1 micron)	Electric voltage separation of charged particles	Continuous	TSI, EAA-3030
Dilution flow	Mass flow meter	Continuous	Matheson, 8163
C ₁ -C ₆ nonmethane	FID chromatography	9 per expt.	Hewlett Packard, 5880A
Light intensity	Continuous stirred quartz reactor (NO ₂ photolysis)	Continuous	Custom

DATA REDUCTION AND ANALYSIS

The analog outputs of most of the instruments were sent to a Fluke 2240A Data Logger and the data were recorded using a Kennedy 1600/36 9-track magnetic tape recorder for processing on a PDP 11/34 computer. A backup system, utilizing strip chart recorders, was used in case the primary data acquisition system fails. Since specialized data reduction and analysis are required, the EAA signals were recorded and processed with TSI's Data Analysis Package, which includes an Apple II Plus Computer. After data validation, the processed data were recorded onto magnetic tape for storage and future availability.

The hydroxyl time profiles for each experiment were determined by monitoring the loss of two different hydrocarbon species that interact differently with HO radicals. However, since alkenes are reactive species, the measured alkene loss was corrected for its reaction with the system's reactive products, such as ozone. On the other hand, the chemical loss of alkane hydrocarbons, in these systems, is primarily due to their reaction with hydroxyl radicals. The reaction of hydroxyl radicals with alkenes is an addition reaction, whereas the reaction of hydroxyl radicals with alkanes is an abstraction reaction. Thus, the use of two different hydrocarbon class compounds allowed the estimation of hydroxyl radical levels in situ utilizing two independent methods. SO_4^{2-} production rate time profiles were determined from aerosol volume measurements which were correlated to SO_4^{2-} mass concentration determined from Teflon filter samples. The procedure used to determine pseudo first order rate coefficients for SO_2 oxidation to SO_4^{2-} from the SO_4^{2-} production time profiles has been described previously by Olszyna et al. (1982). The hydroxyl radical and SO_4^{2-} production time profiles, together with the continuous monitoring of NO_x , O_3 , SO_2 , CO, humidity, light intensity, and temperature, provided valuable information on the chemical mechanisms controlling the atmospheric oxidation processes in power plant plumes.

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APPENDIX B
KINETIC MECHANISM

The mechanism used in the model calculations draws heavily on the work of Atkinson et al. (1982) with modifications as noted. The SO_2 oxidation mechanism developed in this report was substituted for the simple HO-SO_2 chemistry used by these authors.

	Reaction	Rate Constant ppm min units	Notes
1.	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}(^3\text{P})$		1
2.	$\text{O}(^3\text{P}) + \text{O}_2 \rightarrow \text{O}_3$	$6.5 \times 10^3 \text{ T}^{-1}$	2
3.	$\text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	$4.1 \times 10^6 \text{ T}^{-1}$	2
4.	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$1.0 \times 10^6 \text{ T}^{-1} e^{-1450/\text{T}}$	3
5.	$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$		1
6.	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{HO}$	$1.0 \times 10^8 \text{ T}^{-1}$	2
7.	$\text{O}(^1\text{D}) + (\text{O}_2 + \text{N}_2) \rightarrow \text{O}(^3\text{P})$	$1.3 \times 10^7 \text{ T}^{-1}$	2
8.	$\text{HO} + \text{NO} \xrightarrow{\text{M}} \text{HNO}_2$	$8.7 \times 10^8 \text{ T}^{-2}$	3
10.	$\text{HO} + \text{CO} \xrightarrow{\text{O}_2} \text{CO}_2 + \text{HO}_2$	$1.3 \times 10^5 \text{ T}^{-1}$	3
11.	$\text{HO} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$7.0 \times 10^5 \text{ T}^{-1} e^{-940/\text{T}}$	3
12.	$\text{HNO}_3 + h\nu \rightarrow \text{HO} + \text{NO}_2$		1
13.	$\text{HNO}_2 + h\nu \rightarrow \text{HO} + \text{NO}$		1
14.	$\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2$	$3.7 \times 10^6 \text{ T}^{-1}$	3
15.	$\text{HO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2\text{NO}_2$	$1.5 \times 10^8 \text{ T}^{-2}$	3

	Reaction	Rate Constant ppm min units	Notes
16.	$\text{HO}_2\text{NO}_2 \xrightarrow{\text{M}} \text{HO}_2 + \text{NO}_2$	$7.8 \times 10^{15} \text{ e}^{-10420/\text{T}}$	3
17.	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	$3.4 \times 10^4 \text{ T}^{-1} \text{ e}^{1100/\text{T}} +$ $5.8 \times 10^{-5} \text{ T}^{-2} \text{ e}^{5800/\text{T}} [\text{H}_2\text{O}]$	2
18.	$\text{H}_2\text{O}_2 + \text{h}\nu \rightarrow 2\text{HO}$		1
19.	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$	$5.3 \times 10^4 \text{ T}^{-1} \text{ e}^{-2450/\text{T}}$	3
20.	$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	$8.4 \times 10^6 \text{ T}^{-1}$	3
21.	$\text{NO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{N}_2\text{O}_5$	$3.1 \times 10^7 \text{ T}^{-1} \text{ e}^{-1100/\text{T}}$	3
22.	$\text{N}_2\text{O}_5 \xrightarrow{\text{M}} \text{NO}_2 + \text{NO}_3$	$3.5 \times 10^{18} \text{ e}^{-12280/\text{T}}$	3
23.	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$1.33 \times 10^{-3} \text{ T}^{-1}$	3
24.	$\text{NO}_3 \rightarrow \text{NO}$		1,4
25.	$\text{NO}_3 \rightarrow \text{NO}_2 + \text{O}(^3\text{P})$		1,4
26.	$\text{HO}_2 + \text{O}_3 \rightarrow \text{HO} + 2\text{O}_2$	$4.8 \times 10^3 \text{ T}^{-1} \text{ e}^{-580/\text{T}}$	3
27.	$\text{HO} + \text{C}_3\text{H}_6 \xrightarrow{\text{O}_2} \text{HCHO} + \text{CH}_3\text{CHO}$ $+ \text{HO}_2 + \text{NO}_2 - \text{NO}$	$1.8 \times 10^6 \text{ T}^{-1} \text{ e}^{540/\text{T}}$	3

	Reaction	Rate Constant ppm min units	Notes
28.	$\begin{aligned} &O_3 + C_3H_6 \rightarrow 0.5 \dot{C}HCHO + 0.5 \dot{C}H_3\dot{C}HO \\ &\quad + 0.2 \dot{C}H_2O_2 + 0.2 \dot{C}H_3\dot{C}HO_2 \\ &\quad + 0.3 CO + 0.2 HO_2 + 0.1 HO \\ &\quad + 0.2 \dot{C}H_3O_2 \end{aligned}$	$4.17 \times 10^3 T^{-1} e^{-1963/T}$	5
29.	$HCHO + h\nu \rightarrow 2HO_2 + CO$		1
30.	$\rightarrow H_2 + CO$		1
31.	$\dot{C}H_3\dot{C}HO + h\nu \rightarrow HO_2 + CO + \dot{C}H_3O_2$		1,6
32.	$\rightarrow CO$		1,6
33.	$\rightarrow \dot{C}H_3CO_3 + HO_2$		1,6
34.	$\dot{C}H_2O_2 + NO \rightarrow HCHO + NO_2$	$3.1 \times 10^6 T^{-1}$	3
35.	$\dot{C}H_2O_2 + NO_2 \rightarrow HCHO + NO_3$	$3.1 \times 10^6 T^{-1}$	3
36.	$\dot{C}H_2O_2 + H_2O \rightarrow PRDTS$	$1.5 T^{-1}$	3
37.	$\dot{C}H_3\dot{C}HO_2 + NO \rightarrow \dot{C}H_3\dot{C}HO + NO_2$	$3.1 \times 10^6 T^{-1}$	3
38.	$\dot{C}H_3\dot{C}HO_2 + NO_2 \rightarrow \dot{C}H_3\dot{C}HO + NO_3$	$3.1 \times 10^6 T^{-1}$	3
39.	$\dot{C}H_3\dot{C}HO_2 + H_2O \rightarrow PRDTS$	$1.5 T^{-1}$	3

	Reaction	Rate Constant ppm min units	Notes
40.	$\text{HO} + \text{HCHO} \xrightarrow{\text{O}_2} \text{HO}_2 + \text{CO}$	$4.4 \times 10^6 \text{ T}^{-1}$	3
41.	$\text{HO} + \text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_3\text{CO}_3$	$3.0 \times 10^6 \text{ T}^{-1} e^{-250/\text{T}}$	3
42.	$\text{CH}_3\text{CO}_3 + \text{NO}_2 \rightarrow \text{PAN}$	$2.1 \times 10^6 \text{ T}^{-1}$	3
43.	$\text{PAN} \rightarrow \text{CH}_3\text{CO}_3 + \text{NO}_2$	$1.2 \times 10^{18} e^{-13543/\text{T}}$	3
44.	$\text{CH}_3\text{CO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{O}_2$	$3.1 \times 10^6 \text{ T}^{-1}$	3
45.	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{HCHO} + \text{HO}_2 + \text{NO}_2$	$3.1 \times 10^6 \text{ T}^{-1}$	3
46.	$\text{HO} + \text{C}_4\text{H}_{10} \rightarrow \text{AO}_2$	$8.0 \times 10^6 \text{ T}^{-1} e^{-560/\text{T}}$	3
47.	$\text{AO}_2 + \text{NO} \rightarrow 1.3 \text{ NO}_2 - 0.4 \text{ NO} + 0.9 \text{ HO}_2$ $+ 0.6 \text{ CH}_3\text{CHO} + 0.1 \text{ RCHO} + 0.5 \text{ MEK}$	$3.1 \times 10^6 \text{ T}^{-1}$	3
48.	$\rightarrow 1.7 \text{ NO}_2 - 0.8 \text{ NO} + 0.9 \text{ HO}_2 + 0.15 \text{ HCHO}$ $+ 0.3 \text{ CH}_3\text{CHO} + 0.1 \text{ RCHO} + 0.3 \text{ CH}_3\text{COCH}_3$	$3.1 \times 10^6 \text{ T}^{-1}$	3
49.	$\text{HO} + \text{RCHO} \xrightarrow{\text{O}_2} \text{RCO}_3$	$9.2 \times 10^6 \text{ T}^{-1}$	3
50.	$\text{RCO}_3 + \text{NO}_2 \rightarrow \text{PPN}$	$2.1 \times 10^6 \text{ T}^{-1}$	3
51.	$\text{PPN} \rightarrow \text{RCO}_3 + \text{NO}_2$	$1.2 \times 10^{18} e^{-13543/\text{T}}$	3

	Reaction	Rate Constant ppm min units	Notes
52.	$\text{RCO}_3 + \text{NO} \rightarrow \text{C}_2\text{HSO}_2 + \text{NO}_2$	$3.1 \times 10^6 \text{ T}^{-1}$	3
53.	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \xrightarrow{\text{O}_2} \text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$	$3.1 \times 10^6 \text{ T}^{-1}$	3
54.	$\text{RCHO} + \text{h}\nu \xrightarrow{\text{O}_2} \text{C}_2\text{HSO}_2 + \text{CO} + \text{HO}_2$		1,3
55.	$\text{HO} + \text{MEK} \xrightarrow{\text{O}_2} \text{XO}_2$		
56.	$\text{XO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{CHO} + \text{CH}_3\text{CO}_3$	$4.4 \times 10^6 \text{ T}^{-1} \text{ e}^{-330/\text{T}}$	3
57.	$\text{CH}_3\text{CO}_3 + \text{CH}_3\text{CO}_3 \rightarrow 2\text{CH}_3\text{O}_2$	$3.1 \times 10^6 \text{ T}^{-1}$	3
58.	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + 0.66 (\text{HO}_2 + \text{PRDTS})$	$1.4 \times 10^5 \text{ T}^{-1}$	7
59.	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{PRDTS}$	$2.6 \times 10^6 \text{ T}^{-1}$	2
60.	$\text{HO} + \text{SO}_2 \xrightarrow{\text{O}_2, \text{H}_2\text{O}} \text{HO}_2 + \text{H}_2\text{SO}_4$	$1.18 \times 10^{13} \text{ T}^{-4}$	8
61.	$(\text{O}_2) \xrightarrow{\text{O}_2} \text{HSO}_5$	$1.8 \times 10^{11} \text{ T}^{-4}$	8
62.	$\text{HSO}_5 + \text{NO} \rightarrow \text{NO}_2 + \text{HSO}_4$	$3.05 \times 10^6 \text{ T}^{-1}$	8
63.	$\text{HSO}_4 + \text{HO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{O}_2$	$7.63 \times 10^4 \text{ T}^{-1}$	8

	Reaction	Rate Constant ppm min units	Notes
64.	$\text{HSO}_4 + \text{O}_3 \rightarrow \text{HSO}_5 + \text{O}_2$	$3.05 \times 10^3 \text{ T}^{-1}$	8
65.	$\text{CH}_2\text{O}_2 + \text{SO}_2 \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{SO}_4 + \text{HCHO}$	$3.0 \times 10^4 \text{ T}^{-1}$	3
66.	$\text{CH}_3\text{CHO}_2 + \text{SO}_2 \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{SO}_4 + \text{CH}_3\text{CHO}$	$3.0 \times 10^4 \text{ T}^{-1}$	3
67.	$\text{SO}_2 \rightarrow \text{Wall loss}$		9
68.	$\text{O}_3 \rightarrow \text{Wall loss}$		9
69.	$\text{H}_2\text{SO}_4 \rightarrow \text{Wall loss}$		9

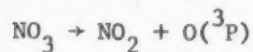
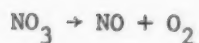
NOTES

1. Chamber Photolysis Rates - The following relative photolysis rates are used for the TVA smog chamber.

Photodissociation Reaction	Relative Rate
$\text{NO}_2 \rightarrow \text{NO} + \text{O}(^3\text{P})$	1.0
$\text{HONO} \rightarrow \text{HO} + \text{NO}$	1.8×10^{-1}
$\text{HNO}_3 \rightarrow \text{HO} + \text{NO}_2$	4.6×10^{-4}
$\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$	9.7×10^{-2}
$\rightarrow \text{NO}_2 + \text{O}(^3\text{P})$	3.2×10^{-1}
$\text{HCHO} \rightarrow 2\text{HO}_2 + \text{CO}$	4.3×10^{-3}
$\rightarrow \text{H}_2 + \text{CO}$	2.6×10^{-3}
$\text{CH}_3\text{CHO} \rightarrow \text{HO}_2 + \text{CO} + \text{CH}_3\text{O}_2$	1.5×10^{-4}
$\rightarrow \text{CO}$	4.1×10^{-4}
$\rightarrow \text{CH}_3\text{CO}_3 + \text{HO}_2$	7.6×10^{-5}
$\text{O}_3 \rightarrow \text{O}(^1\text{D})$	6.0×10^{-2}
$\text{H}_2\text{O}_2 \rightarrow 2\text{HO}$	1.4×10^{-3}

2. Data from NASA (1979) evaluation of atmospheric rate data.
3. Reaction and rate data including any parameterization from Atkinson et al. (1982).

4. NO₃ Photolysis



Photolysis rates are derived from the data of Magnotta and Johnston (1980).

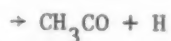
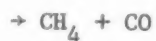
5. O₃ + C₃H₆ Reaction

This reaction is treated explicitly as described by Atkinson et al.; however, the rate constant used was

$$k = 4.17 \times 10^3 / T e^{-1963/T}.$$

This is an average of three independent measurements--Herron and Huie (1974); Becker et al. (1974); and Adeniji et al. (1981)--which are in good agreement.

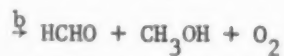
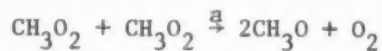
6. Acetaldehyde Photolysis



Quantum yield for these processes are taken from Horowitz and Calvert (1982).

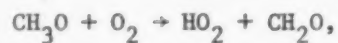
7. CH₃O₂ + CH₃O₂

Parkes (1975) and Parkes (1977) suggest the following mechanism:

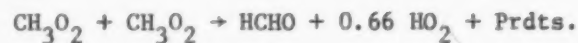


with $k_a/(k_a + k_b + k_c) = 0.33$.

If we assume routes b + c are equally important and that CH_3O becomes HCHO via



the overall reaction can be written



The rate constant is that recommended by Atkinson and Lloyd (1984).

8. See Table 8 of this report.

9. Chamber Dependent Parameters

$$\text{O}_3 \text{ wall loss} = (1.6-1.9) \times 10^{-3} \text{ min}^{-1}$$

$$\text{SO}_2 \text{ wall loss} = (3.3-7.5) \times 10^{-4} \text{ min}^{-1}$$

$$\text{SO}_4^{2-} \text{ wall loss} = (1.0-1.9) \times 10^{-3} \text{ min}^{-1}$$

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